Corrosion

devoted entirely to

CORROSION

Research and Control

CONTENTS

THIS MONTH'S COVER

● *Low Lift Pumping Section of the South District Filtration Plant, City
of Chicago. Every known method of corrosion control applicable to the
Water Industry is utilized by the City of Chicago to reduce corrosion's
toll, thereby reducing the cost of water to the consumer—the taxpayer.
Pumps and other equipments—even the buildings housing them—are
constructed or fabricated of corrosion-resistant materials. Cathodic
protection is utilized on washwater tanks, etc., and chemicals, harm-
less to consumers, are injected into the water to lessen the corrosiveness
of the water to iron pipes of the distribution system. Chicago's efforts
are representative of the Water Industry's fight to cut down an esti-
mated $40,000,000 annual loss suffered by the Industry, and directly
attributable to corrosion. See page 367.*

Statistical Analysis of Test Containers

For Condensate Well Corrosion Studies*

By V. V. Kendall*

THE HISTORY of the high-pressure gas corrosion problem in gas condensate wells has been quite brief. When first discovered in a well in the Opelika, Texas, field in 1942, there was no indication that this type of corrosion was of particular importance to the gas condensate industry as a whole. However, it soon developed that such corrosion was very widespread and the amount of capital investment involved made it of primary importance. Following a period of investigative work by the individual companies concerned, both the Natural Gasoline Association of America and the National Association of Corrosion Engineers decided upon an investigation of the problem. In order that work would not be duplicated, a cooperative arrangement was consummated, whereby NGAA would sponsor the fundamental investigation and NACE the field testing of materials. The U. S. Bureau of Mines at Bartlesville, Oklahoma, was also enlisted in the work. The field testing program of NACE was developed by its Condensate Well Corrosion Committee and, in particular, the Metallurgical Subcommittee.

A program of testing metals, alloys, and other materials in the flow lines of condensate wells was decided upon. Various designs of test containers and of test specimens were considered. Two types of test specimens were finally chosen: one, a washer-type specimen mounted on a rod inserted in the pipe container, the other, a cylinder-type specimen fitting snugly in the pipe container so that the inside wall of the specimen was on a line with the inside wall of the gas flow-line. Before proceeding with the testing of the various materials, it was deemed advisable to determine the variability due to the type of test specimen and the number of replicates of each material that should be used. Therefore, for the first trial period of 90 days, the specimens tested were all of the same steel.

The washer test was installed in the flow line of well No. 1, Gray Account 2, Ohio Oil Co., Cotton Valley Field, La., on May 9, 1945, and removed on September 10, making an actual test time of 112 days, 13 days of which were under "no flow" conditions. The cylinder test

★ A paper presented at the Annual NACE Meeting in Chicago, Ill., April 7-10, 1947.
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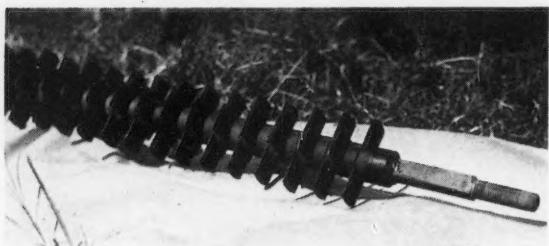
Figure 1—Washer specimens assembled on rod.

was installed in the Gray Account No. 2 well in the same field on December 21, 1945, and was removed March 26, 1946, making a test time of 95 days. This container was lost in shipment for eight months. When finally located, it showed no ill effects from its long sojourn with the railroad.

In the washer test, the specimens were cut from 14-gauge mild steel strap, 1.5 inches wide by 4.4 inches long, with a square hole stamped in the center to fit closely on a $\frac{7}{8}$-inch square steel bar covered with a baked plastic coating. These were placed at right angles to each other and separated by insulating washers. The container was ten feet long and contained 129 specimens. Eight non-test specimens 0.45-inch longer than the test specimens were placed in pairs at intervals of one-third of the way along the bar, to act as weight-carrying specimens to prevent the test coupons from touching the pipe wall. Figure 1 shows one end of the specimen bar and Figure 2 shows the container installed in

the flow-line. It is obvious that with this arrangement, the turbulence factor is tremendously accelerated.

The idea upon which the cylinder test was based was to reproduce the actual gas flow conditions as found in the well tubing without accelerating any single factor. The inside diameter of the test specimen was therefore the same as the inside diameter of the well tubing. Figure 3 is a sketch showing the salient features of the container. The container was 2½-inch double extra-strong pipe, six feet long with reducing flanges to 2 inches double extra-strong pipe. The specimens were cylinders, 2 inches long seamless tubing, with an inside diameter of 1.510 inches which was on a line with the inside diameter of 1.503 inches of the well flow-line. They were separated from each other by bakelite rings, 0.25 inch wide, of the same diameter as the specimens. They were also separated from the pipe wall by an insulating baked synthetic resin coating, which had
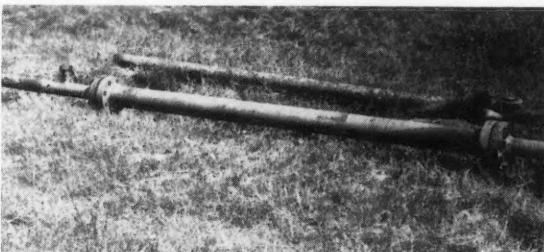
Figure 2—Washer test container installed in flow-line.

CYLINDER – TYPE SPECIMEN CONTAINER

SPECIMEN $\begin{cases} O.D. \ 1.750" \\ I.D. \ 1.510" \end{cases}$

INSULATING BAKELITE SPACER

$2\frac{1}{2}"$ DOUBLE EXTRA STRONG PIPE, COATED

REDUCING FLANGE

2" DOUBLE EXTRA STRONG PIPE I.D. 1.503"
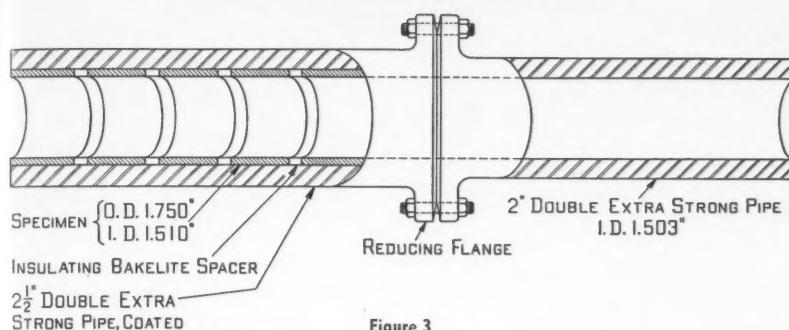
Figure 3

been applied to the pipe. This container held 30 specimens.

The results of the washer test are shown in Figure 4, where loss in weight is plotted against position in the container. It is apparent that the results are subject to wide variation. It is also apparent that there is a downward trend in the weight-loss from the gas inlet to the gas outlet end of the container. The tremendous volume of gas passing through the container precludes the hypothesis of a decrease in corrosive constituents in the gas to explain this phenomenon. The most reasonable hypothesis seems to be a progressive change in turbulence conditions from one end of the container to the other.

It is quite evident, as expected, that the data will fall on a straight line. The regression line was therefore calculated by the least squares method.

$$Y = a + bX$$

where Y = estimated weight loss of specimen
$\quad$ X = position of specimen
$\quad$ a = constant
$\quad$ b = regression coefficient or slope of line

The standard deviation of the weight losses is calculated by,

$$\sigma_y = \sqrt{\frac{\Sigma x^2}{N-1}}$$

The standard error about the regression line is calculated by,

$$\sigma_{xy} = \sqrt{\frac{\Sigma y^2 - \frac{(\Sigma xy)^2}{\Sigma x^2}}{N-2}}$$

In both formulas, x and y are deviations from the mean.

According to statistical theory, if
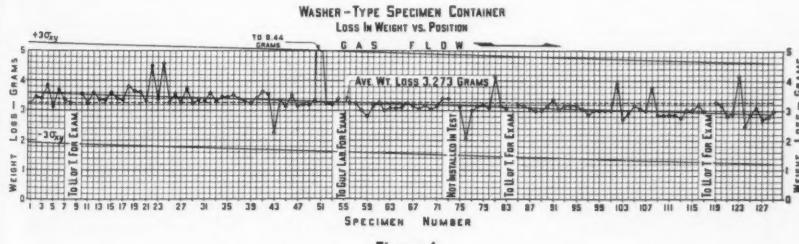
Figure 4
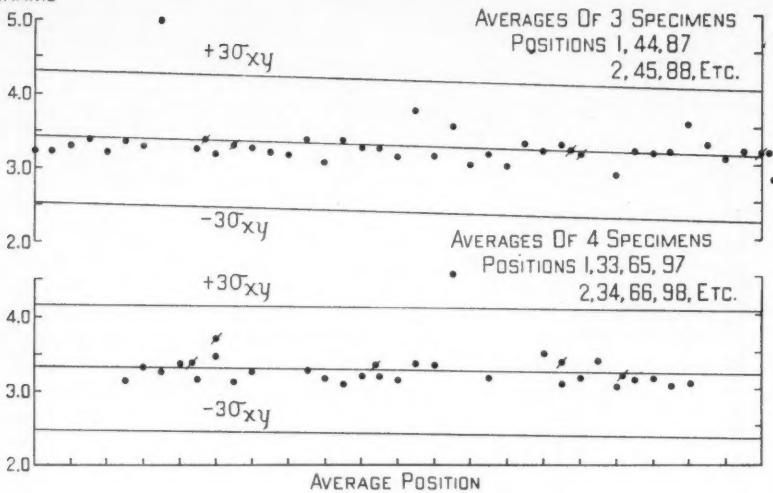
Fig. 5

the variation of the data is due to chance alone, 99.73 percent of the data will fall within the limits of three times the standard deviation, or three times the standard error measured plus and minus from the regression line. If, therefore, the points fall outside of these limits, it is due to some cause other than chance variation. The closer the points are grouped about the regression line, the better is the control. In this case, while there is only one point outside of the control limits, there are quite a number of points a considerable distance from the regression line and the limits are excessively large. The data as a whole are subject to large variation. The standard error is plus or minus 17 percent from the mean or a range of 34 percent.

The question now arises, how much can we decrease the standard error by using the averages of more than one specimen? The container was divided into sections, the number of sections corresponding to the number of specimens to be averaged. For an average of two specimens, Nos. 1 and 65, 2 and 66, etc. would be used: for three specimens, Nos. 1, 44 and 87; 2, 45 and 88, etc. The results for averages of from two to eight specimens are given in the table. (Page 366). Figures 5, 6, and 7 are graphical presentations of the control resulting from the use of three to eight specimens.

Some inconsistencies may be noted in the table and graphs. These are due to the fact that loss in weight data on five specimens, which were used for further examination, were missing. These points are indicated by a 45° line drawn through

CONDENSATE WELL CORROSION PROBLEM
WASHER TEST

Fig. 6

CONDENSATE WELL CORROSION PROBLEM
WASHER TEST

Fig. 7
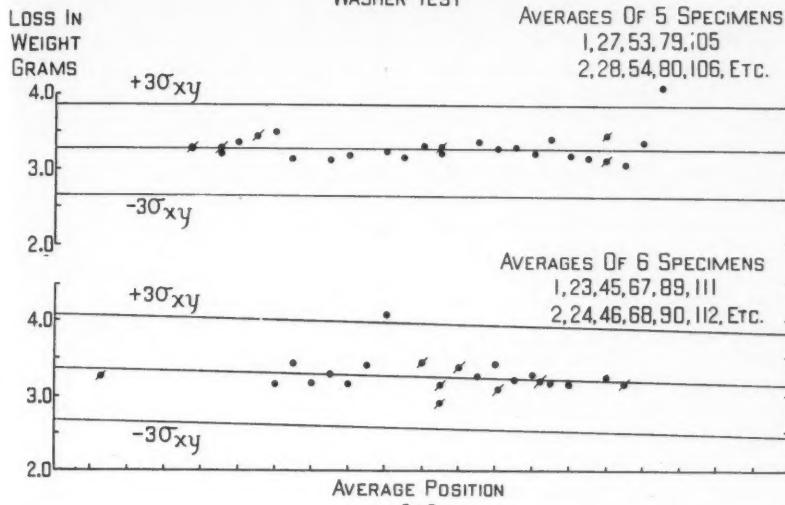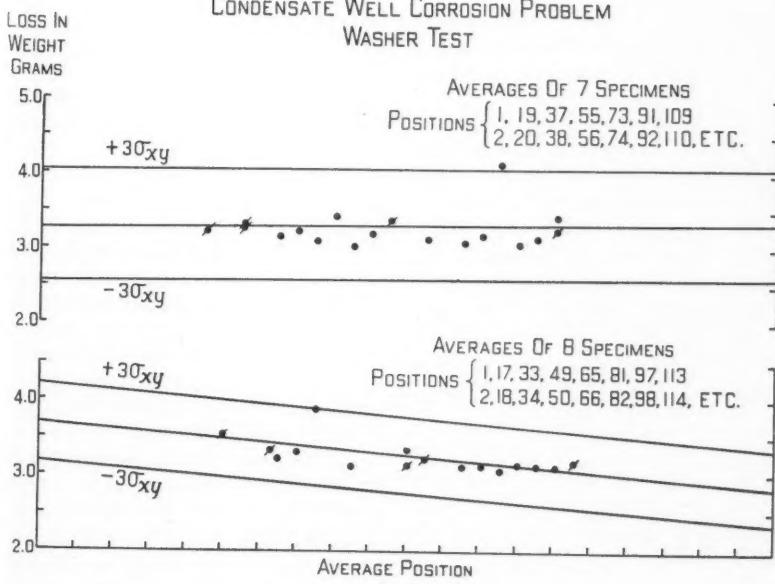
the point and represent averages of one less than the number given. It was also necessary, in some cases, in order to obtain the proper grouping, to omit end points. The effect of the missing specimens, in general, seems to be minor with the exception of the slope obtained for averages of eight specimens. In this case, the majority of the values averaged in the first two points were much higher than the average and the last point was much lower, with the result that the slope became very steep.

The standard error steadily decreases from 17 percent for single observations to 5.22 percent for averages of eight observations. Missing specimens, or omitting specimens, in order to obtain the proper grouping apparently had an effect on the averages of six and seven specimens. It should be noted that the one point out of control, which had a value of 8.436 grams, could not be brought under control by any amount of averaging. The standard deviation of the weight losses is within 1 percent of the standard error. All of the variation in the data can therefore be explained on the basis of experimental error with the exception of the one point, 8.436 grams.

The same procedure was used in analyzing the data for the cylinder test. The standard error for all specimens was ± 3.95 percent of the mean. When the four high values at the inlet end of the container were omitted, the standard error was 3.07 percent. This is illustrated in Figure 8. These higher values were due to the turbulence effect as there was some interruption of straight line gas flow through the flange opening. However, these values were not sufficiently high to throw any of the averaged points out of control. Only the first specimen is close to the three-sigma line.

A downward slope through the container is noted when all specimens are plotted. This disappears when the first four values are omitted. As a matter of fact, it is only necessary to omit the first two specimens to remove the turbulence effect at the inlet. Calculations for averages of from two to six specimens are given in the table, and illustrated in Figure 9. In the case of averages of four specimens, Nos. 1 and 2 were omitted
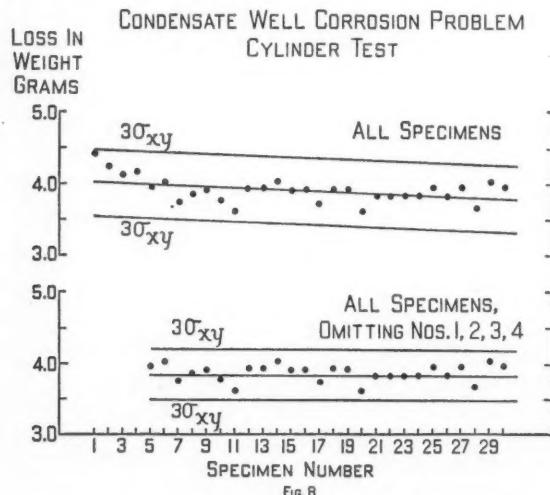
CONDENSATE WELL CORROSION PROBLEM
CYLINDER TEST

Loss In Weight Grams

Fig. 8

CONDENSATE WELL CORROSION PROBLEM
CYLINDER TEST
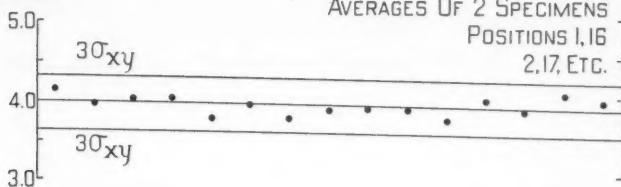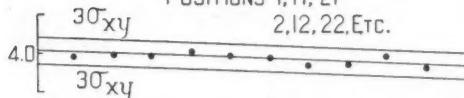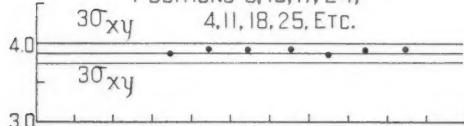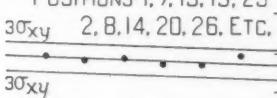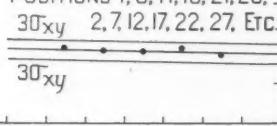
Fig. 9

in order to obtain complete groups. The standard error decreases from 3.95 percent for all specimens, to 1.09 percent for six specimens.

No comparison can be drawn between the rate of corrosion in the two containers because they were installed in separate wells.

In the design of any experiment, it is necessary to consider the amount of variation in the results that can be permitted in view of the purpose for which the results will be used. For example, an increase in life of 25 percent for any tubing material for a condensate well would not justify a change to that material, particularly when its probable increased cost is considered. Therefore, a com-

paratively high standard error in testing the material could be allowed. Furthermore, the cost of preparing additional specimens can be saved if the additional specimens do not add a significant amount to the accuracy of the experiment. In the case of the washer test, four specimens of each material could be used with an expected error of 8.64 percent. This was the number of replicates finally decided upon for the follow-up test with this container. When the cylinder container was reported lost, it was decided to proceed with the washer container for the current test. For that reason it is not now under test.

STATISTICAL ANALYSIS – SUMMARY
WASHER-TYPE SPECIMEN

SUBGROUPS	NUMBER OF GROUPS	STANDARD DEVIATION OF WEIGHT LOSSES σ_y % OF MEAN	STANDARD ERROR σ_{xy} % OF MEAN	REGRESSION EQUATION
ALL SPECIMENS	124	17.95	16.98	$Y = 3.619 - .00532\ X$
AVERAGES OF 2 SPECIMENS	64	11.77	11.68	$Y = 3.485 - .00329\ X$
" " 3 "	43	9.40	9.11	$Y = 3.735 - .00711 \cdot X$
" " 4 "	32	8.50	8.64	$Y = 3.484 - .00313\ X$
" " 5 "	26	6.23	6.07	$Y = 3.277 - .00001\ X$
" " 6 "	22	6.88	6.96	$Y = 3.598 - .00507\ X$
" " 7 "	18	7.25	7.48	$Y = 3.281 - .00012\ X$
" " 8 "	16	6.36	5.22	$Y = 4.622 - .02088\ X$

CYLINDER-TYPE SPECIMEN

SUBGROUPS	NUMBER OF GROUPS	STANDARD DEVIATION OF WEIGHT LOSSES σ_y % OF MEAN	STANDARD ERROR σ_{xy} % OF MEAN	REGRESSION EQUATION
ALL SPECIMENS	30	4.27	3.95	$Y = 4.047 - .00776\ X$
ALL SPECIMENS OMITTING NOS. 1,2,3,4.	26	3.02	3.07	$Y = 3.862 + .00064\ X$
AVERAGES OF 2 SPECIMENS	15	3.01	2.92	$Y = 4.076 - .00946\ X$
AVERAGES OF 2 SPECIMENS OMITTING NOS. 1,2.	14	1.88	1.95	$Y = 3.870 + .00012\ X$
AVERAGES OF 3 SPECIMENS	10	1.88	1.34	$Y = 4.217 - .01805\ X$
" 4 " NOS. 1,2, OMITTED	7	0.84	.92	$Y = 3.893 - .00011\ X$
AVERAGES OF 5 SPECIMENS	6	1.57	1.53	$Y = 4.190 - .01640\ X$
" 6 "	5	0.99	1.09	$Y = 4.042 - .00740\ X$

Conclusions

Our statistical analysis of the data from the washer and cylinder test container has developed the following:

1) The standard error for 124 specimens in the washer test was plus or minus 17 percent of the mean. Four specimens each of 32 materials can be tested with an expected error of 8.64 percent.

2) The corrosion rate decreases from the gas inlet to the gas outlet end of the washer container, the equation for which has been calculated.

3) The standard error for 30 specimens in the cylinder test was 3.95 percent of the mean. By using blank specimens in the No. 1 and No. 2 positions, thereby removing the turbulence effect at the inlet end in the gas flow due to the flange, two specimens each of 14 materials can be tested with an expected error of 2 percent.

4) There is no significant change in corrosion rate from one end of the cylinder container to the other.

Corrosion Costs to the Water Industry*

By Harry E. Jordan*

BECAUSE THE COMMODITY which the public water supply industry distributes is, in its natural state, corrosive to the metallic equipment and installations used to produce and transport it, it becomes a natural necessity that steps be taken either to reduce the corrosivity of the product or to protect the equipment and installations from corrosion.

It may be termed an anomaly that the conditions under which water supply is delivered are predominately affected by the use to which only a minor fraction of the production is put. The one-half gallon per day which each consumer of the water utility's product may drink or use in his food, governs to a major extent the methods used to produce the supply and to bring it to that consumer in a state of safety.

Added to safety is the requirement that the taste and odor of the product be inoffensive to the person who drinks it.

The life of many a water works executive is plagued by the dim recollection that many of his customers have of a spring or a well from which they drank in their childhood. They remember a sort of sparkle in the water, and they also remember the zest with which they drank from that spring or well on a summer's day. What they do not remember (if they ever knew it) is that the water was probably not safe, and that it would not have complied with the standards which are today imposed upon and voluntarily accepted by the water supply industry. What they also probably do not know is that the well or spring water, if it had a sparkle, was a corrosive water. Likewise, they probably do not know that the water, if transported through miles of conduits and mains, would not keep that sparkle. The chances are that the sparkle will be changed to a corrosion product in the mains, or that today the water purveyor would remove or effectively reduce it before the water entered the main.

It would be possible to reduce the corrosivity of water to a greater degree than is currently practiced if the consumer's daily half-gallon did not have to be mixed up with the balance of the 133 gallons per day which public water works produce for all uses to which their customers may put them. In other words, corrosion control methods cannot be used in producing water supplies if the treatment used makes the water unsafe for human consumption, or

if it gives the water a taste or odor the consumer will not consider acceptable.

Size of Industry

In 1940, there were approximately 81,500,000 persons in the U. S. who were served by public water supplies. The normal rate of urban growth is such as to add 500,000 persons per year to the connected load of water works. Thus in 1947, there are at least 85,000,000 persons using public water service in the U. S.

The industry has invested more than $5,000,000,000 in this service and collects for it more than $500,-000,000 annually. In the long term, approximately 300 tons of metal are required for the service of each 1000 persons connected to a water system. For the long term maintenance and repair needs of the water utility, nearly 5 tons of metal are required annually per 100 persons served. For the production, purification and pumping of the supply, less than 10 percent of the installed metal is required. The more than 90 percent remaining is required to transport the water from the works to the customers. This, incidentally, means up to the property of the customer only. We shall not discuss the piping installations in factories, office buildings and residences.

The cost of the distribution system of the average water works amounted to $40.00 per capita, or two-thirds of the $60.00 average prewar (II) water works investment in the U. S. While the use of steel and asbestos cement as water distribution materials is increasing, the great bulk of water distribution systems in the U. S. today consists of cast-iron pipe and cast-iron accessories. In the closing quarter of the last century, a substantial amount of ferrous metal other than cast-iron was used in constructing the distribution systems of American water works. These materials were not of the high quality now produced and their protective coatings were insufficient to block off the attack of the water upon the metal. Consequently many miles of mains so seriously failed in service as to require their replacement. It is reliably estimated that by 1940 there had been installed more than 24,-000,000 tons of cast-iron pipe, valves, hydrants and fittings in the U. S. water systems. It is this mass of cast-iron to which we propose to give much attention.

Corrosion of Pipe

The pipe in this assembly has traditionally been coated with what in trade terms is called a "tar-dip." This material is of uncertain composition, has not been reliably standardized, and the present-day product appears to have less protective value than its antecedent material of 50 or more years ago. It provides a type of protection for the outside of the pipe which has been reasonably adequate in normal soils. As an internal coating material, it affords only secondary protection. As a result, the adverse effects of corrosion of water mains in dollar terms have been very substantial. These adverse effects have not been, as some might expect, of such a nature as to perforate or destroy a great proportion of the pipe.

More than 90 percent of the original cast-iron pipe installed in the U. S. remains in service. But its ca-

pacity to transport water has deteriorated. The adverse effects lie in the reduction of hydraulic capacity derived from the tuberculation of the inside of the pipe, i.e., the retarding of the flow of the water by the roughness or reduction of effective area of the channel. Wilson, of the Pitometer Company,[1] evaluated this loss in carrying capacity in midwestern waters at about 1 percent per year. Howson has computed this loss at "50 cents per capita per year, or nearly 10 percent of the gross revenue of the average water utility."[2] A simple projection of this per capita loss would amount to more than $40,000,000 per year—which might be assumed to be the annual amount charged to corrosion of water mains in the U. S. today. The true total is somewhat less than this, although there does not appear a reasonable basis for fixing a definite dollar amount. Whatever the total may be, it is a significant charge against the water users, and merits such improvement of practices as will reduce it.

Restoring Capacity

The first corrective step is cleaning the pipe. There are over the country many miles of pipe which have been in service 50 years and more, but these are today incapable of delivering the amount of water which the customers wish to use, or if delivering the required amount, they do so at a substantially increased cost of energy for pumping. The report on Pipe Line Friction Coefficients[3] made by the N.E.W.W.A. Committee (1935) under Elson Killam's leadership, concludes that:

"(1) Cleaning will ordinarily restore the main to approximately 85 percent of its original capacity.

"(2) The effectiveness of restoring capacity depends primarily upon the original cause of capacity loss, i.e., whether it was due to tuberculation, incrustation, mud or slime. Tests indicate that restoration is more effective in tuberculative mains than mains choked by incrustation or lime deposits.

"The degree of restoration depends also upon the thoroughness with which cleaning is performed and the extent to which tuberculation has been allowed to progress. There are indications that mains with unusually low coefficients before cleaning, say C equals 20 to 30, are never restored to as high capacity as mains that are in better condition.

"(3) The relatively high capacity observed immediately after cleaning, may be lost rapidly, particularly in the case of small mains. Rate of capacity loss depends on the cause of loss and the relative activity of the water. The rate will ordinarily be quite steep in comparison with the original trend.

"(4) Cleaning is an important preliminary step to more permanent methods of restoring and maintaining capacity. Among these methods are: the introduction of corrective treatment and the lining of mains in place."

Howson has shown that the prewar cost of main cleaning was approximately 5 percent of the cost of the installed pipe new. Postwar price levels, both for labor and materials, are such as probably to reduce the percentage cost of cleaning old mains

in comparison with the cost of installation of new lines.

It is presumed that it is not necessary to describe in detail the methods used to clean water mains. Several companies are prepared to remove the tuberculation or sludge deposits from pipe lines by the use of water-propelled or cable-drawn scrapers. The cost of the operation is, as above cited, only about one-twentieth of the cost of a new line of equal diameter.

Can this restored capacity be maintained? Not in general—unless the pipe is relined in place. Can this be done? To a large degree, it can. Small diameter pipelines—4, 6, 8 and 12 inches or more—can be relined in place with cement, by the Tate process, or with a bituminous material, by the Eric process. Although the Eric process has been used in England for several years, there has as yet been no application of it to municipal water lines in the U.S.* Pipelines 24 inches and larger can be relined by several methods, utilizing the application of either cement or tar-enamel. Large lines have been successfully relined by use of the modern coal-tar enamel types of coatings, whose early efficiency gives promise of long life with high hydraulic capacity.

Analysis of a number of water systems in terms of "length of pipe of various diameters installed" discloses the interesting fact that approxi-

* The application of this process is now being promoted in the United States. It involves cleaning the interior of the pipe and filling the section with a water emulsion of bitumen. Current is applied to an electrode which is drawn slowly through the emulsion-filled main. The bitumen is deposited on the pipe wall in a coating which becomes firmer and protects the metal against corrosion. The life expectancy of the coating cannot now be estimated.

mately 85 percent of the previously installed pipe in U. S. water systems has a diameter of 4 to 12 inches inclusive; and only about 10 percent of the total length of installed pipe is 24 inches in diameter and over. In terms of installed tonnage, the smaller diameter pipe makes up over 50 percent of the total and the larger diameter pipe, 40 percent.

At present, methods of relining of lines (in place) 16, 18 and 20 inches in diameter (inclusive) are not known to the author. This middle ground amounts, in terms of length, to only 5 percent, and, in terms of weight, to only 10 percent of the total installed.

Relining small lines in place with cement consists of isolating sections from service; serving customers through specially laid temporary lines; cleaning the inside of the pipe by use of the conventional scraper type equipment; and then drawing a cement mixture into place by use of a special mandril. The procedure requires intelligent planning, and patience. The result is a cement-lined pipe which is subject to little corrosion and tuberculation, and whose carrying capacity remains at a high level for a long period.

Costs of Relining

Prewar costs for cleaning and relining 4, 6 and 8-inch lines in busy streets of small cities amounted to slightly over $1.30 per foot of pipe. Two-thirds of this cost was for the actual cleaning and relining, and one-third for service line disconnection, trenching, paving, and by-pass installation. Under more favorable traffic conditions and longer experience, total costs of such relining

dropped to $1.00 per foot and less under prewar conditions. This is substantially less than the cost (one-half more or less depending upon conditions) of installing new lines and has the major virture of conserving metal already installed. Some sample 1947 prices at San Diego, Calif., are $2.64 per foot for 10-inch pipe, and $2.74 for 12-inch pipe.

The cleaning and relining of larger lines—24 inches in diameter and over —likewise has been found fully effective and economical. Costs vary with the diameter of the pipe and the conditions under which the work has to be done. In lines of large diameter, however, a cleaning and relining project is bound to be in sharp competition with the costs of installation of a new line. It is safe to say that no large diameter line is relined when the cost of relining is not substantially less than the cost of a new line in place.

The losses in flow capacity, the costs of pumping due to tuberculation, and the economics of cleaning and relining at least 95 percent of the length of pipe installed in the U. S. water systems are so clear that it is difficult to accept the deliberation with which the corrective measures are being applied.

Installing Protected Pipe

In recent years, the cast-iron pipe industry has developed and promoted the installation of cement-lined pipe. About 40 percent of the cast-iron pipe sold today for water works use is cement-lined. Wolfe, of the Cast Iron Pipe Research Association, has shown how, in areas where half the hydraulic capacity of the tar-dip lined pipe had been lost after 10 years of service, the capacity of cement-lined pipe remained unimpaired after 15 years of service.

In an interesting tabulation of the relative costs of a 30-inch cement-lined pipe and a 36-inch tar-dipped pipe. He also shows that the service rendered by the smaller diameter cement-lined pipe will, over a 45-year period, be superior to the service rendered by the larger diameter tar-dipped line, and the cumulative cost of pumping an equivalent amount water will be less in the smaller cement-lined pipe than in the larger tar-dip lined pipe.[4]

The reluctance with which many water works engineers accept the 10 percent or more additional cost of purchasing a water main pipe which is adequately coated and lined with the modern tar-enamel or cement lining cannot be justified. Under modern labor conditions, the cost of the small diameter pipe itself is the lesser element in the total cost of installation. In addition, if the engineer takes into consideration the performance of the pipe line throughout its useful life and the year after year capacity to deliver water under satisfactory power costs and service conditions, the case for the adequately protected metal is very clear and convincing.

We have shown that the principal component of the water system, the distribution mains, suffers a capacity loss due to corrosion approximating 50 cents per person served per year. We have shown that the major portion of the already installed water mains can be cleaned and relined economically and the hydraulic capacity of the relined mains maintained for many years. We have shown that the cast-iron pipe indus-

try is prepared to furnish its product with a lining that will maintain capacity satisfactorily. Steel pipes with the modern tar-enamel or concrete linings likewise appear capable of long service with little loss of capacity. Asbestos-cement pipe shows little evidence of capacity loss due to corrosion and promises a satisfactory service life.

Assuming that the materials have been properly coated or lined, what of reducing the tendency of the water to corrode materials with which it comes in contact?

Reducing Corrosivity

It may be granted that in the earlier days of water treatment (as it was designed to clarify the water and make it safe to drink) methods and materials used tended to increase the corrosivity of the product. The U. S. Public Health Service made a survey of water treatment as of 1940.[5] A total of 5372 treatment plants were recorded which served 74,308,000 persons. The processes listed included not alone rapid or slow filtration, but softening, iron and manganese removal, corrosion control, and simple chlorination.

Out of the total number of treatment systems then in service, the following procedures may be presumed to reduce or to be able to reduce the corrosivity of the water:

Iron and manganese
   removal 456
Softening 258
Combination of above.....138
Corrosion control not with
   above 73
                               ————
   Total 925

Without referring in detail to operations of some of the above types of plants where corrosivity may not now be controlled, we may assume that all of these plants could, with adjustments in treatment methods based upon present knowledge, deliver water whose corrosive character would be adequately reduced. The fact that less than 20 percent of the treatment plants in the U. S. in 1940 applied processes definitely intended to reduce the corrosive character of the supply indicated that, just as there is much to be done in reducing the exposure of the pipe metal to the corrosive effect of water, there are also many water systems which should be applying corrosivity reducing treatment to the water itself.

Since Langelier's work[6] on equilibrium conditions in water, the fundamentals of corrosion control have been increasingly known. Reduction of carbon dioxide and adjustment of pH by addition of lime makes for corrosivity reduction, and the cost is not excessive. In recent years, the use of the glossy phosphates has been widely studied. Application of amounts up to 2.0 ppm. appears to serve as a mechanism to control the corrosive tendencies in many waters. The net cost of such treatment should not exceed $2.00 per million gallons —not a serious addition to the cost of producing a water supply—but a substantial contribution to reduction of the over-all cost of water supply operation and maintenance, if we take into account the saving which will be brought about by the extension of the useful life of the water mains at the capacity for which they were installed.

It appears safe to assume that the industry is at the threshold of a

new era in controlling the losses which corrosion inflicts upon it. There are many miles of water mains in service today whose capacity to deliver can be restored by cleaning. After cleaning, most of this pipe can be relined in place so that its hydraulic capacity will remain at a high level. New mains can be installed in cast-iron with concrete lining in steel with tar-enamel lining, or in asbestos-cement (each in the place where it is best fitted for use), but all protected against loss of capacity due to corrosion.

Finally, the industry is on the verge of widely applying the knowledge it has been gaining in recent years, by making adjustments in the treatment processes of such nature as to deliver to the pumps and mains a product whose tendency to corrode has been reduced to a practical minimum. The materials and the methods are available. The time has come to use them.

The writer makes no claim of having conducted the various studies upon which this discussion is based. Killam and his associates in the N.E.W.W.A. study, Wolfe acting on behalf of the Cast Iron Pipe Research Association, Howson in his many fine studies of the economics of water supply, Moore and his A.W.W.A. Committee on Corrosion Control, Langelier, Hoover, Hale, Rice, Pallo, Barbee, Hurlbut, Hayes and many others have studied the various problems derived from the corrosive effects of water upon public water supply installations.

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Chemical Reaction in Metal Protective Paints*

By E. J. Dunn, Jr.*

I N THIS symposium on corrosion resistant paints considerable data have been presented in regard to various formulas for specific purposes. One of the basic reasons there are so many formulations is that the drying and weathering of a paint film is a complex subject. It seems simple but the drying of a linseed oil paint may involve more than two-score different chemical reactions. There is the oxidation reaction with subsequent formation of peroxides, aldehydes, ketones and short chain aliphatic compounds. Hydrolysis of the oil or dried film may take place to produce free fatty acids and diglycerides. Various types of polymers are formed. Esterfication of free fatty acids, neutralization of the short chain aliphatic compounds, some reaction with the atmospheric elements and complex soap formations. From this partial list of chemical reactions it is evident how tremendously complex is the simple phenomena of drying and weathering of a paint film.

One of the more widely used paint vehicles is linseed oil. Linseed oil if spread as a thin film by itself gives poor protection and has a relatively short life. It is like rubber, it usually is reinforced. Consequently, it is never used alone. If a clear linseed oil film were used by itself it might give some protection for about a year. Adding a completely non-reactive white or inert pigment might give protection for eighteen months. By adding the proper amount of reactive pigment to the formation, good protection may be obtained from four to eight years in atmospheric exposure.

When a pigment reacts with the vehicle it forms what is known as soaps. In an attempt to determine what soap formations are, what they look like and how they form in a linseed oil or the fatty acids of linseed oil, we started some microscopical studies many years ago. It was soon evident that soap formations existed in many forms and were produced at varying rates and in varying amounts depending on the compound mixed with the vehicle. Not all compounds are capable of forming soaps. For instance, in metal protective paints and primers there

Figure 1—Lead soaps—polarized light.   Figure 2—Red lead soaps—transmitted light.
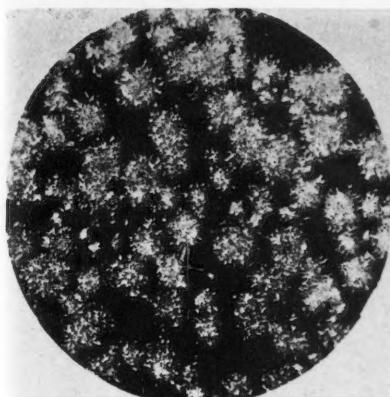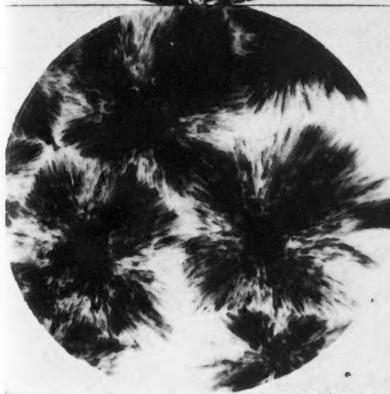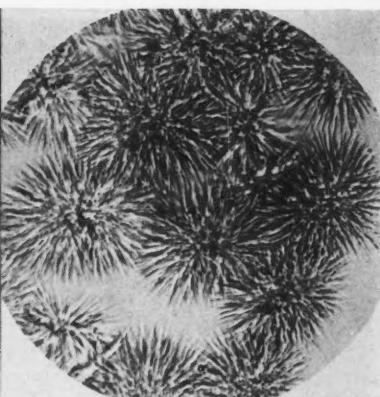
Figure 3—Lead soap—colored transparency.   Figure 4—Zinc soaps—polarized light.
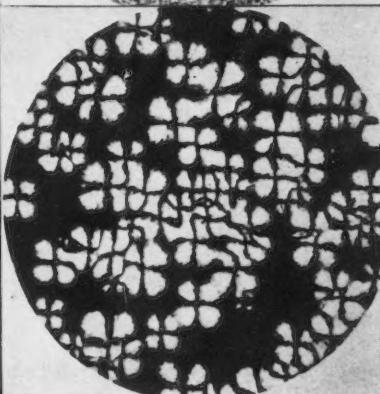
is little tendency for aluminum flake or iron oxide to react with the vehicle whereas red lead, basic lead chromate or zinc oxide will form soap readily.

Lead soaps form a series of radiating rods growing out from a central core. Figure 1 illustrates a type of lead soap formation as it appears by polarized light. Polarized light as you may know is obtained in a petrographic microscope when the nicols are crossed. When the nicols are crossed no light goes through unless an anisotropic substance is mounted on the stage. These particles are formed by precipitation from solution within the oil. These soap particles in unrestricted growth are of larger particle size than the usual particles of pigment.

Figure 2 is another stage of growth

in the formation of lead soap particles. It is very evident from these pictures how these particles intertwine and would mechanically reinforce the film. This type of particle growth is somewhat analogous to fibers in cloth. Ordinarily fibers are relatively short pieces of material with little strength, but once they are woven together their strength is increased many times. Lead soap particles also have the characteristic of being able to pull apart into a multitude of small individual rods. This is beneficial as once the elastic limit of the dry film is exceeded the soap particles will pull apart and thereby produce a fine type of microscopical break and avoid large ruptures.

Figure 3 is a black and white reproduction of a colored transparency of red lead soap particles in fatty acids of linseed oil, taken with polarized light using colored film to record the image. It is a further illustration how these particles intermesh and would mechanically reinforce the film. These soap formations were prepared with the fatty acids of linseed oil but are very similar to the soap formations obtained with raw linseed oil. Fatty acids usually give a better type of growth for the display purposes.

Zinc Soaps

Zinc oxide is another pigment that reacts with the vehicle and forms soap. Figure 4 is an illustration of the formation of zinc soaps in polarized light. Zinc soaps usually form an identifying cross under polarized light such as is observable in the photomicrograph. By comparing this picture with the lead soap pictures it

Red Lead
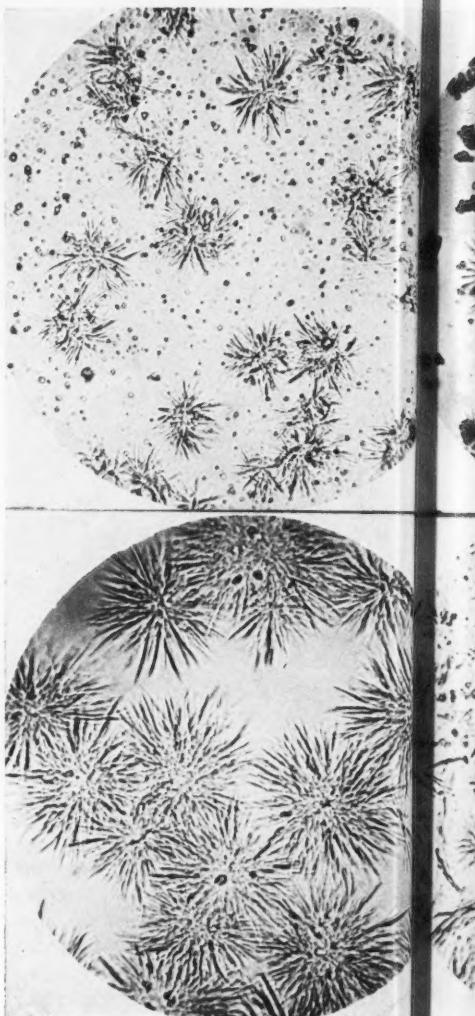
Basic Lead Carbonate

Figure 5—Lead soap formation 4

Basic Lead Chromate
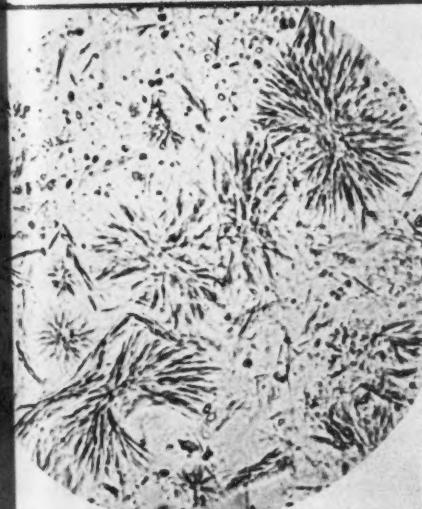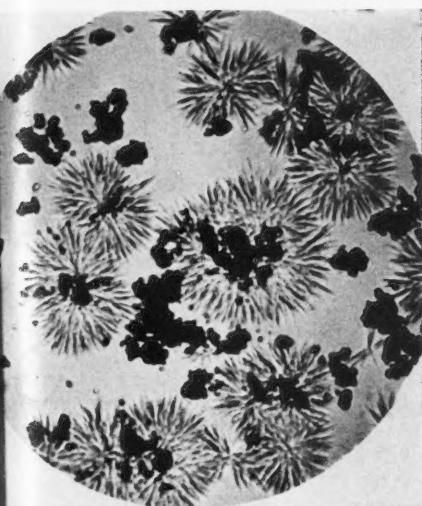
Basic Lead Silicate

formication 400X.

is evident that the zinc soaps produce a more solid crystalline formation. It is believed these particles add hardness to the film. The fact that some paint films have the tendency to fail by cracking while other films fail by chalking or fine checking, we believe is closely associated with these minute chemical reactions products.

Before concluding these microscopical pictures of soaps it would be well to point out that in general all lead compounds produce practically the same type of soap particle. Figure 5 shows four different lead soap formations. The red lead soap has not developed quite to the extent of the other soap formations but it has formed the radiating rods. Dark particles or specks in the background are the particles of pigment. In the tri-basic lead chromate soap formation the bushy type soap particle is more evident. The dark opaque particles in this photomicrograph are the particles of basic lead-chromate grouped together. In this form they stop the passage of light and, therefore, appear black. Similarly, the basic lead silicate and basic lead carbonate soap formations are of the rod type radiating out from a central core. There is some difference in appearance but basically all these photomicrographs show the same general structure.

There are several ways in which these soap particles may form, namely: 1) The structures may form by direct addition of the basic pigment with the fatty acid present in the oil. 2) Hydrolysis of the oil or dry film may take place to produce diglycerides and free fatty acids which would then react as mentioned
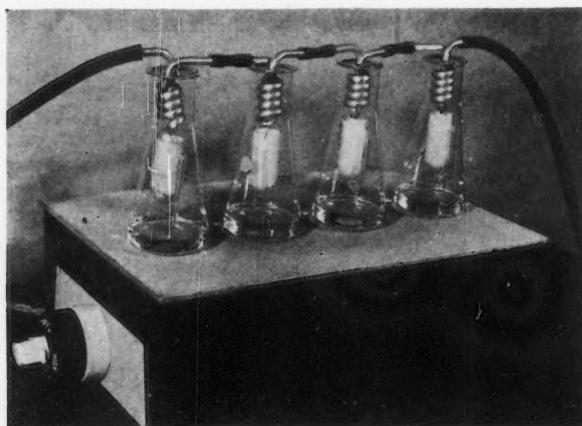
Figure 6
Extraction
apparatus.

above. 3) A reaction between the basic pigment and the short chain acidic decomposition products formed on oxidation. 4) When a film polymerizes and oxidizes new ester groups may be formed. Hydrolysis of these new ester groups will also produce acids which may react with the basic pigment. 5) There is some controversy as to the basic pigment joining up at the double bonds present in a drying oil. Our studies in this direction are not complete, but it appears as a possibility on the basis that the clear oil at the top of aged air tight containers of paint shows a pronounced reduction in iodine value with accompanying increase in acid number and metallic soap content. There are five possible reactions and there probably are others.

Chemical Determination of Soap Formations

After studying these formations microscopically experiments were undertaken to determine chemically the amount of soap formed in the container of paint and also within the paint film as it ages and weathers. Portions of the paint in the container and portions of the dried aged film were extracted with a refluxing apparatus as shown in Figure 6. A solvent consisting of equal molar parts of benzol and ethyl alcohol was used for the extractions.

Extraction of the dried paint film required special preparation. The paint films were spread with our automatic doctor blade using tin-coated copper or tin-coated iron as the base material. After the paint films dried two months indoors the tinned panels were amalgamated with mercury and the paint film stripped from the base. Approximately five gms of the stripped film were placed in the extraction thimble and the soluble portion extracted over a 10-hour refluxing period.

Analyses have been made for the respective metallic contents of a series of single pigment raw linseed oil paints. Table I illustrates the metallic contents calculated to a linoleate.

There are several things of inter-

TABLE I

Acid Number and Soap Determinations on Raw Linseed Oil Paints and Dried Paint Films Aged Two Months Indoors

Name of Pigment	% Soap as Linoleate		Acid No. of Extracted		Acid No. Clear Oil
	Paint	Film	Paint	Film	
Red Lead	Pb 4.45	11.4	20.8	38.0	18.9
Chromated Red Lead	Pb 1.21	2.1	22.8	51.0	6.1
	Cr 0.03	0.22			
Pb_3O_4 + $PbCrO_4$	Pb 0.14	4.32	12.6	30.0	5.1
	Cr --	--			
Zinc Chromate	Zn 0.22	1.79	8.85	50.4	1.3
	Cr 0.08	1.34			
Iron Oxide	Fe 0.09	0.05	9.8	63.7	0.3
Aluminum Flake	Al 0.08	0.12	9.7	57.5	3.0
Pigment X	Ba 0.04	--	13.4	48.1	0.7
	K 0.4	3.6			
	Cr 0.21	0.59			
$PbCrO_4$ · 3 PbO	Pb 3.7	8.7	19.3	32.9	19.5
	Cr 0.03	0.11			
Zinc Oxide	Zn 0.31	14.3	3.7	52.1	0.9
White Lead	Pb 0.04	3.4	4.1	58	0.7
Raw Linseed Oil				60	3.0

est to be noted in Table I. First, it may be observed that in general very little metallic soap is formed in the container. White lead has 0.04 percent soap in the paint, zinc oxide 0.31 percent and similarly the chromium, potassium, or barium contents are relatively small for the paint in the containers. Red lead, chromated red lead and tri-basic lead chromate have formed slightly larger quantities of soap in the container. The tri-basic lead chromate is of a higher degree of basicity than is used for metal protective primers but is included in this series to help establish the trend of results.

When the quantities of soap formed in the container are compared with the quantities of soap obtained in the dry paint film aged two months it is apparent that appreciably more soap is formed within the paint film as it ages. In these tests zinc oxide has formed approximately 50 times the quantity of soap found in the con-

tainer. Red lead and tri-basic lead chromate have formed considerable soap, but all the other reactive pigments form a relatively small amount of soap by comparison. Iron oxide as you see forms practically no soap either in the paint or the aged paint film. Similarly, aluminum flake shows practically no reaction with the vehicle. All these values should be considered as a trend of results. They are not exacting values and the quantities formed vary with conditions. Therefore, the results should be thought of as comparative for this series of tests and typical of the trend of soap formation reactions.

It is a most fortunate phenomenon that the bulk of the soap forms in the film as it ages and weathers. When the soaps form in the paint film it is forming where it will produce the most good.

After a paint film has dried and set there are still many chemical reactions taking place. The oil film continues to oxidize which in turn sets free some short chain acidic compounds as well as splitting off some fatty acids from the tri-glycerides by hydrolysis. These products tend to liquefy or soften the film. Some paint systems actually become gummy to the extent they can not be handled during this softening period. Reactive pigments within the film will slowly unite or combine with these decomposition products of the vehicle and prevent this extreme softening of the film. This slow formation of lead soaps within the film as the film ages actually enhances the life of the paint film.

From this tabulation of data it is also evident that zinc chromate has formed a comparatively small amount

of soap both in the paint and the paint film considering zinc as a reactive pigment. Chromium may have a tendency to restrict soap formation. Zinc oxide forms appreciable soap within the film but zinc chromate forms little soap. Red lead forms appreciable soap within the film but a mixture of red lead and normal lead chromate forms little soap. E pigment which is a barium potassium chromate forms only a small amount of soap within the film. The above chromates are practically neutral compounds which may have less tendency to react than the basic compounds and, therefore, would naturally tend to produce less soap. However, the fact that the soap is less than might be expected with some of these compounds indicates chromium may have a restraining effect on soap formation.

Acid Number Determinations

Acid number determinations have been made on all the paints in this series as well as the acid number determinations on the extracted dried paint films. These acid number determinations were made to try to note the speed of reaction or rate of neutralization of the acids within the paint film. The criterion would be the higher the quantity of soap formed and the lower the acid number of extracted film, the greater the speed of reaction. For comparison the acid number of clear raw linseed oil film aged two months was 60. Looking at this table as a whole it is evident that the acid number of the dried paint films increased materially as the paint films aged. The acid number of the original raw linseed oil in the paints was 3, while the average

TABLE II

Permeability of Raw Linseed Oil Films After Adding Various
Lead Soaps on the Basis of 5% by Volume

Lead Soap Added	Pigment Vehicle-Ratio	*Film Permeability	**Specific Permeability
Raw Linseed Oil (Clear)	--	1199	3.04
Mono-basic Lead Phthalate	5	1090	2.78
Lead Treated (Pb)	5	1250	3.17
Lead Napthanate	5	1230	3.12
Lead Linoleate	5	1199	3.04
Lead 2 Ethyl Hexoate	5	1208	3.07
Lead Phthalate Stearate	5	1360	3.46
Normal Lead Phthalate	5	1208	3.06
Red Lead	30	415	1.05

* Film Permeability
  mgs of water per 10 sq cm per 1 mil thickness per 1 day

** Specific Permeability
  mgs of water per 1 sq cm per 1 mm thickness per 1 day

As paint films age the permeability to water decreases so that the formation of soap within the film may aid the further restriction of the passage of water. However, the major restriction to the transfer of water appears to be due to other factors. Just what the mechanism of water permeability amounts to is hard to say but the mechanical interference of the pigment, its film compaction, the amount of water a film picks up and holds within the film, the vapor pressure and the water solubility of the film no doubt all affect the permeability.

acid number of raw linseed oil or raw linseed oil with inert pigment combinations is in the range of 55 to 65. In general, the reactive pigment paint films have lower acid numbers than the non-reactive pigments. The soap formation does counteract some of the acidity. However the acids are formed at a faster rate than the soap reactions proceed as in no case has the acid number been reduced to a point anywhere near the acid number of the original oil.

Water Permeability of Soaps

An attempt was made to deter-mine the effect of soap formations on the water permeability of paint films. If a paint film picks up and holds appreciable water or allows appreciable water to pass through the film it is natural that a rusting or blistering condition has a better chance to ensue. Accordingly, we used various types of lead soaps such as lead linoleate, phthalate, stearates, hexoates as well as forming some lead soaps right in the paint vehicles. These were put in raw linseed oil respectively on the basis of 5 percent by volume. Films were prepared with our automatic inclined

doctor blade on patapar paper and water permeability determined. A red lead, raw linseed oil paint film of 30 PV was used for comparison. Results are as indicated in Table II. From this it is evident that soaps as such apparently have no unusual properties with regards to restricting the passage of water through paint films. Raw linseed oil has a specific permeability of 3.05 while for all practical purposes the film with the various soaps added has about the same permeability. Red lead has a specific permeability of only 1.05 showing it is highly restrictive to the passage of water.

In conclusion, the foregoing has given some conception of one phase of the chemical reactions that take place within the paint film. The phenomenon of lead soap formations and the character of the particles produced actually help to stabilize the paint system. The rate at which the lead soaps are produced in the film is also a most fortunate phenomenon. The acidic decomposition products form in the film at a faster rate than the soap formations proceed as the acid number of the films is never reduced to the acid number of the original paint. An acid number in the range of 70 to 90 is still prevalent in some films that have weathered five years at our Sayville Exposure Station. Without these beneficial chemical reactions it appears paint films would be less durable. It is our experience that chemical activity has to be given consideration in formulating metal protective primers and paints for good durability and adhesion.

A Survey of
High-Temperature, Gas, Atmosphere
Corrosion of Iron-Nickel-Chromium Alloys

Part II

By James T. Gow*

This concludes a survey of the complex problem of hot-gas atmospheric corrosion of iron-nickel-chromium alloys being conducted by J. T. Gow and his associates at Battelle Memorial Institute under the sponsorship of the Alloy Casting Institute. The paper was presented in its entirety during the Annual Meeting of the National Association of Corrosion Engineers in Chicago, Ill., April 7-10, 1947. Part I of the paper appeared in the July, 1947, edition of Corrosion (Vol. 3, No. 7, 311-324).

RECENTLY, Brasunas, Gow, and Harder[11] presented the results of air-atmosphere corrosion tests on a wide range of Fe-Ni-Cr (iron-nickel-chromium) compositions, which showed the trend of change in scaling resistance conferred by chromium and nickel content variation, and the influence of temperature change on the minimum requirements of nickel and/or chromium for assuring a maximum in resistance to metal loss by oxidation scaling.

Specimens 1-inch long by ⅜-inch diameter, machined to a ground finish, were used in test. From weight-change data obtained by descaling the corroded specimens in a molten caustic salt bath, and the surface areas, the metal loss was calculated

in terms of grams per square inch per day. By using an average value for the density of the Fe-Ni-Cr alloys, the corrosion rate was also calculated in terms of inches penetration per year.

Figure 10 is a plot of their data of metal loss by scaling in an air atmosphere saturated with water at 90° F. The exposures were continuous for 100 hours at temperatures from 1600 to 2200° F. The alloys tested represent a wide range of compositions, with the chromium content varying from 11 percent to 31 percent and the nickel content varying from 0.0 percent to a maximum of 70 percent. The specimens were prepared from sand mold castings, and all alloys contained, in addition to iron, nickel and chromium, about 0.4 percent carbon, 1.2 per-

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cent silicon, and 0.8 percent manganese.*

Considering the alloys from the standpoint of the minimum nickel content conferring a near maximum in oxidation scaling resistance at various chromium levels, it is shown by Figure 10 that, in general, a lesser amount of nickel is required as the chromium content is increased from 11 percent toward 26 percent, or as the temperature considered is moderated from 2200° F. to 1600° F. At the chromium levels of 26 percent and 31 percent, however, nickel additions appear to have merit when added in a limited amount, with the optimum being at about 15 percent ± 5 percent nickel. Temperatures ranging from 1600 to 2200° F. are apparently without effect on the optimum minimum nickel content to provide maximum corrosion resistance.

Conversely, considering the alloys from the standpoint of the minimum chromium content required to confer a near maximum in oxidation scaling resistance at various nickel levels, it is shown that, in general, a lesser amount of chromium is required as the nickel content is increased from 0.0 percent to a maximum of 70 percent, or as the temperature is moderated from 2200 to 1600° F. At 60 percent nickel, it is only necessary to increase the chromium content from 11 percent to about 16 percent to have maximum oxidation scaling resistance when the maximum temperature considered increases from 1600 to 2200° F. At 40 percent nickel, maximum scaling resistance at temperatures up to

1600° F. is attained, with but about 11 percent chromium present. At 1800° F., a minimum of about 16 percent chromium is required with 40 percent nickel to have maximum oxidation scaling resistance. At 2000° F. and 2200° F., about 18 percent chromium is the minimum amount of chromium with 40 percent nickel for maximum scaling resistance.

For alloys at the 15 percent nickel level, a minimum of 16 percent chromium is required for having maximum corrosion resistance at 1600° F.; at 1800° F., a minimum of 21 percent chromium is required; while at 2000° F. and 2200° F., a minimum of about 26 percent chromium is required.

In the case of the plain Cr-Fe alloys, a minimum of about 19 percent chromium is required for maximum corrosion resistance at 1600° F.; at 1800° F., about 21 percent chromium; and at 2000° F. and 2200° F., some 26 percent chromium or more is needed to supply maximum corrosion resistance.

It is clearly shown by this investigation that the maximum scaling resistance for Fe-Ni-Cr alloys, when exposed at temperatures from 1600 to 2200° F., can be obtained with a wide range of compositions. In general, as the amount of chromium used in the alloy is increased, the minimum amount of nickel necessary decreases. Conversely, as the amount of nickel used in the alloy increases, the minimum amount of chromium necessary to obtain maximum corrosion resistance decreases. Also, as the temperature requirements are raised, the minimum amounts of chromium and/or nickel

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* Most of the cast alloy materials were prepared by the Research Laboratory of the American Brake Shoe Company.
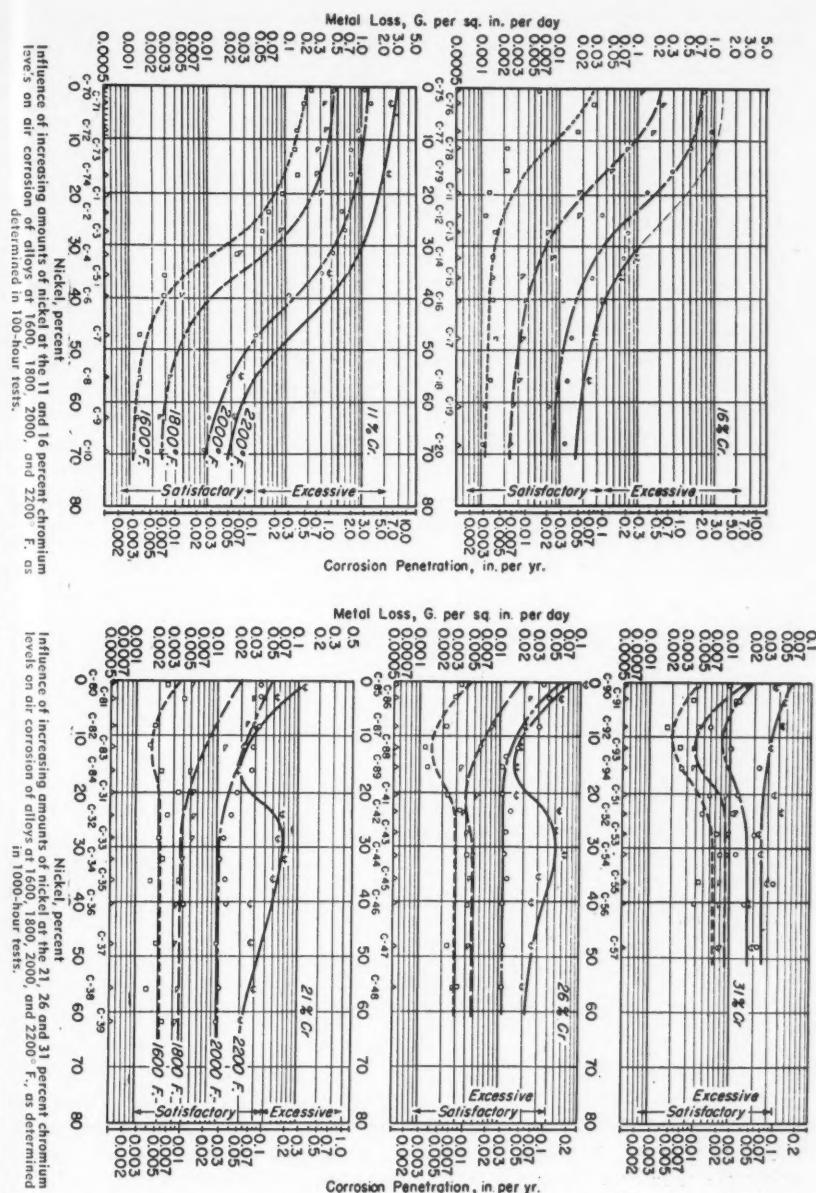
Figure 10. (Brasunas, Gow and Harder: Reference 11.)

required to obtain maximum scaling resistance increase.

These same investigators[11] also studied the influence of a longer time continuous exposure (1000-hour) on the relative scaling resistance of these same alloy compositions. Also, the influence on the relative corrosion resistance of interrupted heating (alternate heating and cooling) and of interrupted heating with the addition of mechanical shock was studied. The data obtained are plotted in Figure 11, in which the corrosion loss is expressed in inches penetration per year, as calculated from the metal loss obtained in the 100-hour test and in the 1000-hour test.

A lesser corrosion penetration in inches per year for the 1000-hour tests than calculated from the 100-hour tests would indicate that an increased protection against scaling was built up in 1000 hours of exposure over that built up in 100 hours. It will be noted that, in general, the rate of metal loss in the 1000-hour continuous test is less than that obtained in the 1000-hour interrupted exposure, and that the 1000-hour interrupted and tumbled exposure conditions resulted in the greatest amount of corrosion.

It is also shown by Figure 11, for alloys with 11 percent chromium and less than 30 to 40 percent nickel, that the scaling rate had decreased with increased exposure time for all three conditions of the 1000-hour test, so that the extent of metal loss indicated to occur in one year, based on the 1000-hour test, is less than that based on the 100-hour test. Alloys wih more than this amount of nickel are indicated to have their corrosion

resistance appreciably damaged by the interrupted heating and tumbling.

In the case of the 16 percent chromium variable-nickel content alloys, the rate of metal loss by scaling decreased at all nickel contents as the exposure time was extended to 1000 hours under conditions of continuous exposure and interrupted heating. Interrupted heating with tumbling is shown to have resulted in an increased scaling rate over that indicated by the 100-hour continuous exposure for alloys with more than 30 percent nickel, but not for alloys with less than this amount of nickel. It is, therefore, indicated that, at chromium levels of 11 and 16 percent, the scale formed on alloys with more than about 30 percent nickel are damaged more severely by mechanical shock than the lower nickel content alloys. Hence, the same extent of improvement indicated to be afforded by increasing nickel contents at these chromium levels by continuous exposure tests of 100-hour and 1000-hour duration is not to be had when conditions of mechanical shock are also involved.

In the case of the 21, 26, and 31 percent chromium alloys, the scale built up during the 1000-hour test is shown to have been capable of being retained to an extent such that the rate of metal loss continuously decreased, so that the average rate over the 1000-hour period was somewhat less than the average rate in 100 hours of test.

It is of importance to note that the rather marked beneficial effects indicated by the 100-hour test to occur at the 21, 26, and 31 percent chromium levels by adding increased amounts of nickel up to 15 or 20 per-
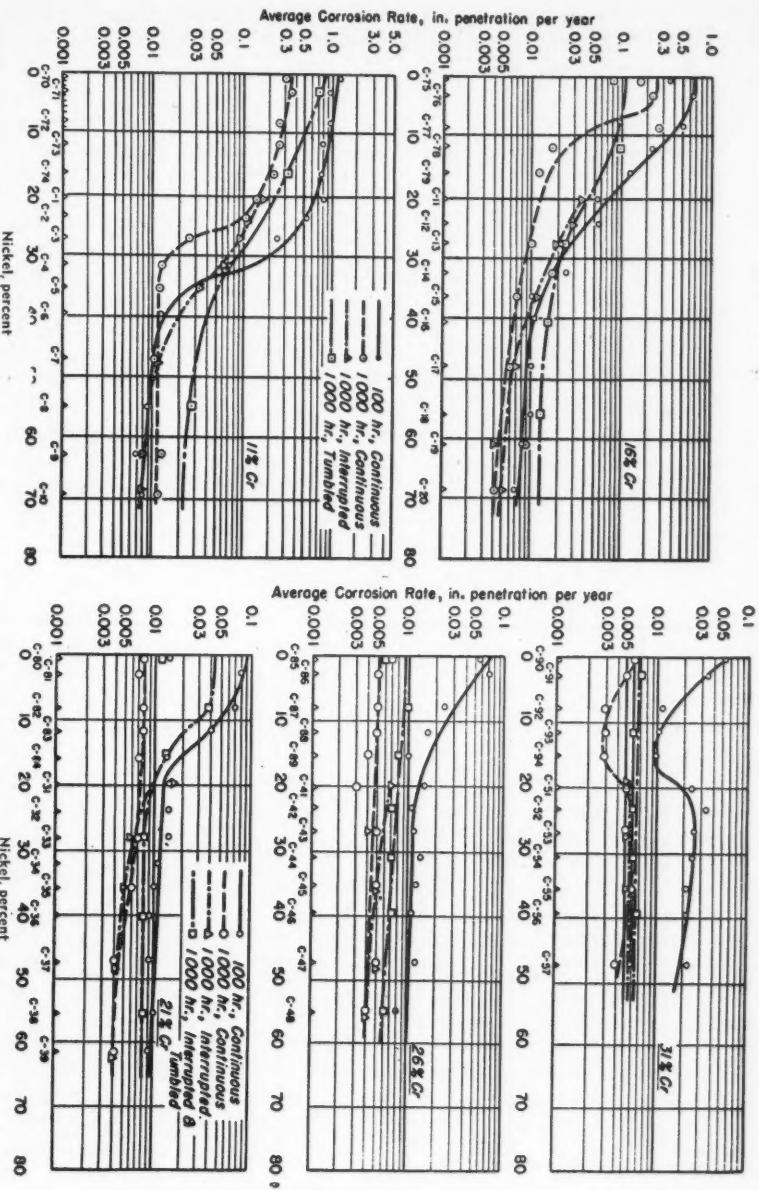
Figure 11. (Brasunas, Gow and Harder: Reference 11.)

Figure 12—Loss of metal by scaling in the interrupted exposure and tumbling test.
(Alloy Casting Institute: Reference 20.)
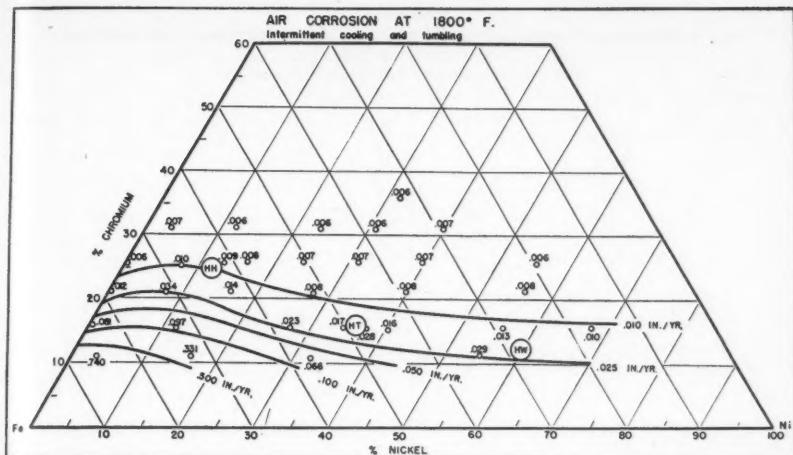
Figure 13—Metal loss by air corrosion at 1800° F. with intermittent cooling and tumbling. Based on 1000-hour tests. Corrosion expressed in "inches per year." (Alloy Casting Institute: Reference 20.)

cent are found, in all but one instance, to be lessened or entirely removed when judged on the basis of the 1000-hour tests. The exception is in the case of alloys with 21 percent chromium subjected to interrupted heating and tumbling.

Discussion of the Interrupted Heating and Tumbling Test

Figure 12 is an interesting plot of the change in weight as followed each day for some of these specimens included in the interrupted heating and tumbling test. The weight loss on descaling the specimens is also shown. It will be noted that, for a number of these alloys, little difference is observed between their weight loss until after 5 to 10 days' exposure. The alloys which showed superior corrosion resistance under this condition of test are shown not only to be the ones which retained their scale well, but the ones

which had formed the lesser total amount of scale in test. The variations among alloys, both in regard to adherence of the scale layer and the relative degree of protectiveness of the adherent scale layer, are evaluated by this test condition of alternate heating and tumbling.

The corrosion data obtained in the interrupted heating and tumbling test were used to arrive at the isocorrosion lines drawn on the ternary Fe-Ni-Cr diagram of Figure 13. The locations of the alloys tested are shown, and the total metal loss by scaling which occurred for each alloy is shown at each alloy location. This figure clearly shows what ranges of alloy compositions have a near maximum in oxidation scaling resistance at 1800° F. under conditions of long-time exposure with alternate heating and cooling and mechanical shock superimposed.

This relatively long-time inter-

TABLE 5

The Composition of Materials Exposed to the Combustion Products of Gas Fuel Burnt with 50% Excess Air

The Corrosion Data Are Given in Figure 14

No.	C, Percent	Fe, Percent	Cr, Percent	Ni, Percent	Si, Percent	Mn, Percent	Other
1	0.25	Bal.	0.04	0.10	0.18	0.48	
2	0.36	Bal.	14.66	0.30	0.26	0.12	
3	0.42	Bal.	7.47	0.19	3.5	0.50	
4	0.13	Bal.	18.65	8.22	0.50	0.33	Ti 0.61 / W 0.63
5	0.40	Bal.	13.65	10.31	0.97	0.41	W 3.53
6	0.23	Bal.	23.20	11.85	1.65	0.41	W 2.98
7	0.34	Bal.	19.16	7.57	1.24	0.69	W 3.98
8	0.40	Bal.	14.85	27.65	2.15	1.25	W 3.83
9	0.14	Bal.	24.35	21.5	1.36	0.29	
10	0.22	Bal.	30.4	0.26	0.69	0.56	
11	0.10	Bal.	13.0	62.0	0.45	1.40	
12	0.07	Bal.	13.44	78.85	0.27	0.21	
13	0.09	1.12	18.72	77.65	0.65	1.24	

(Hatfield: Reference 12.)

rupted heating and tumbling test technique is thought to merit consideration as a standard laboratory technique for use in rapidly evaluating the probable service performance of alloys. It can be readily visualized that different alloy compositions will form scale layers which will be affected to different extents by these factors. Since the adherence of the protective scale layer is of prime importance in controlling the oxidation rate, it is impossible to get a complete evaluation of the merits of an alloy for service applications unless the influence of thermal expansion and contraction and mechanical shock is evaluated in the test performed.

Flue-Gas Corrosion

Hatfield[12] presented results of scaling tests for a series of alloys exposed to the products of combustion of town gas. The gas was burned with 50 percent excess air over that required for complete combustion. The composition of the alloys tested is given in Table 5. The test was designed to include the influence of repeated heating and cooling. The specimens were cooled down to room temperature between each six hours of exposure to the scaling conditions, and the test consisted of seven complete cycles. Each specimen was cooled beneath an inverted beaker after each cycle of exposure, and weighed with any scale which flaked off. The loose scale was brushed off before replacing the specimen in the furnace. This procedure was repeated for the seven cycles, and the total increase in weight, expressed in milligrams per square centimeter of surface, was reported. The results obtained can probably be taken as being typical of what would be obtained in the combustion product of low-sulfur-content fuels. These results are given in Figure 14.

It is shown by Figure 14 that different alloys scaled to different degrees at a given temperature and also responded differently to increasing temperatures. Some alloys are shown to pass from useful to useless resistance with but a small temperature change.

The line X — X' was placed on this figure to give a very approxi-

TABLE 6

Hot-Gas Corrosion in an Industrial Furnace at 1940° F.
(50% Operation With Natural Gas and 50% With Fuel Oil)

| HEAT No. | CHEMICAL ANALYSIS, PERCENT | | | | | | Total Test Period, Hrs. | Avg. Corrosion Rate, In./Yr. |
	C	Ni	Cr	Si	Mn	N		
HT-14	0.14	34.7	16.4	1.2	0.72	0.05	8100	0.135
HT-35	0.35	34.9	16.0	1.3	0.67	0.05	8100	0.235
HT-44	0.44	34.9	16.4	1.2	0.74	0.05	8100	0.210
HT-47	0.47	34.9	16.0	1.2	0.82	0.04	5150	0.125
HT-56	0.56	34.8	15.9	1.3	0.80	0.04	5150	0.163
HT-61	0.61	34.6	16.1	1.3	0.76	0.05	5150	0.173
HT-70	0.7	34.7	16.5	1.3	0.81	0.05	5150	0.155
Avg.								0.171
HH-32	0.32	12.8	26.7	1.2	0.54	0.16	8100	0.155
HH-31	0.31	11.2	28.7	1.2	0.55	0.16	8100	0.095
C-4	0.35	31.8	11.1	1.3	0.82	0.04	2110	0.390
C-14	0.45	32.2	16.0	1.2	0.80	0.08	2110	0.120
C-16	0.46	40.3	16.0	1.2	0.80	0.08	2110	0.070
C-34	0.47	32.3	20.9	1.2	0.77	0.07	2110	0.040
Avg.								0.125

(Avery: Reference 13.)

mate indication of the gain in weight in this test, which would be equivalent to a loss of metal of 0.10 inch per year.

Plain steel (No. 1) is shown to withstand temperatures up to about 1100° F. satisfactorily. Also, Alloys 2 (14% Cr steel) and 5 (14% Cr-10% Ni) are useful up to 1500° F. Alloy 4 (18.6% Cr-8.2% Ni) could be used successfully up to about 1650° F. The useful range for Alloys 3 (7.5% Cr-3.5% Si), 7 (19.2% Cr-7.6% Ni-4% W), and 11 (13% Cr-62% Ni) is up to about 1850° F. Alloy 6 (23% Cr-11.8% Ni-3% W) is possibly moderately superior to the aforementioned alloys. Alloys 8 (14.8% Cr-27.6% Ni-3.8% W), 9 (24.4% Cr-21.5% Ni), and 10 (30.4% Cr-0.3% Ni) appear safe for use up to about 2000° F., while Alloys 12 (78.8% Ni-13.4% Cr) and 13 (77.6% Ni-18.7% Cr) are indicated to be of practical value at 2200° F.

Avery[13] recently reported the results of corrosion data ob-
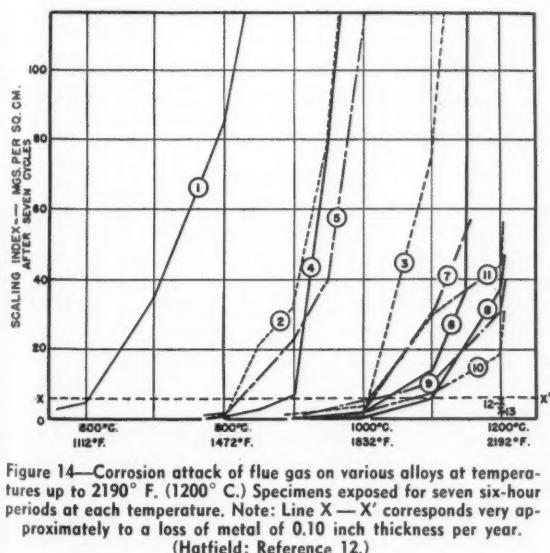
Figure 14—Corrosion attack of flue gas on various alloys at temperatures up to 2190° F. (1200° C.) Specimens exposed for seven six-hour periods at each temperature. Note: Line X — X′ corresponds very approximately to a loss of metal of 0.10 inch thickness per year. (Hatfield: Reference 12.)
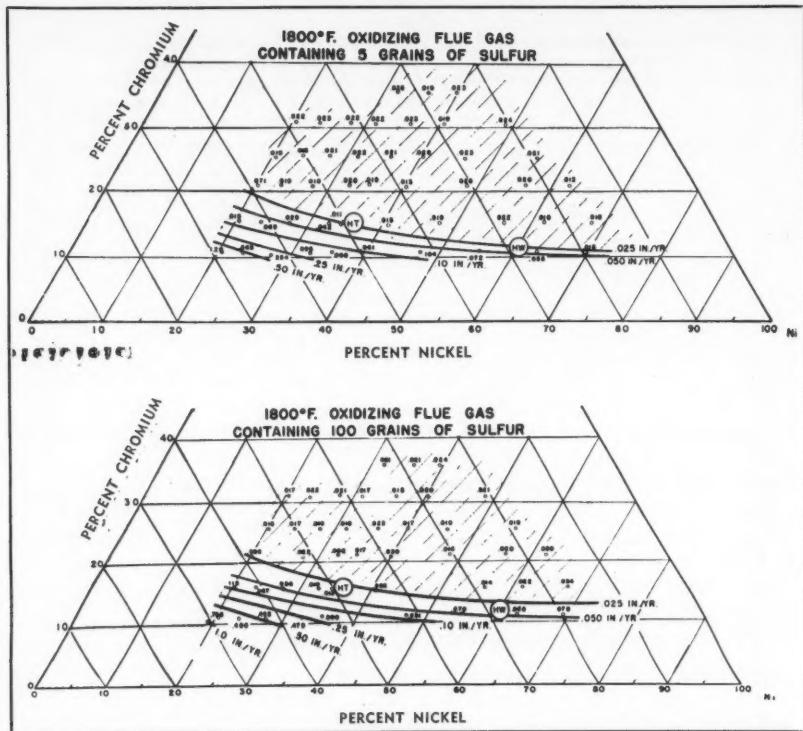
Figure 15—Influence of alloy content on extent of corrosion penetration per year as indicated by 100-hour tests at 1800° F. in oxidizing flue gas containing sulfur. Alloys also contain 0.4 percent C, 1.25 percent Si, 0.75 percent Mn. (Alloy Casting Institute: Reference 14.)

tained from field tests made under industrial service conditions which are of value in showing the benefits derived from increased amounts of chromium. Table 6 gives these data. In this test, the alloys were exposed for periods ranging from 2100 to 8100 hours in a furnace operating intermittently at 1940° F. The furnace was fired about one-half the time with natural gas, which would be essentially sulfur free, and for about one-half of the time with fuel oil. He mentioned that a comparison test was made of the corrosion occurring in the

periods of 100 percent gas firing, with that resulting when oil was used about one-half of the time, which showed that more severe corrosion was encountered with the latter condition. This would be expected, owing to the moderate sulfur content of the fuel oil. The group of alloys, C-4 to C-34, which are identical in composition with the alloys included in the Alloy Casting Institute program, demonstrates the definite benefit to be derived by increasing the amount of chromium from 11 to 21 percent at the 32 percent nickel
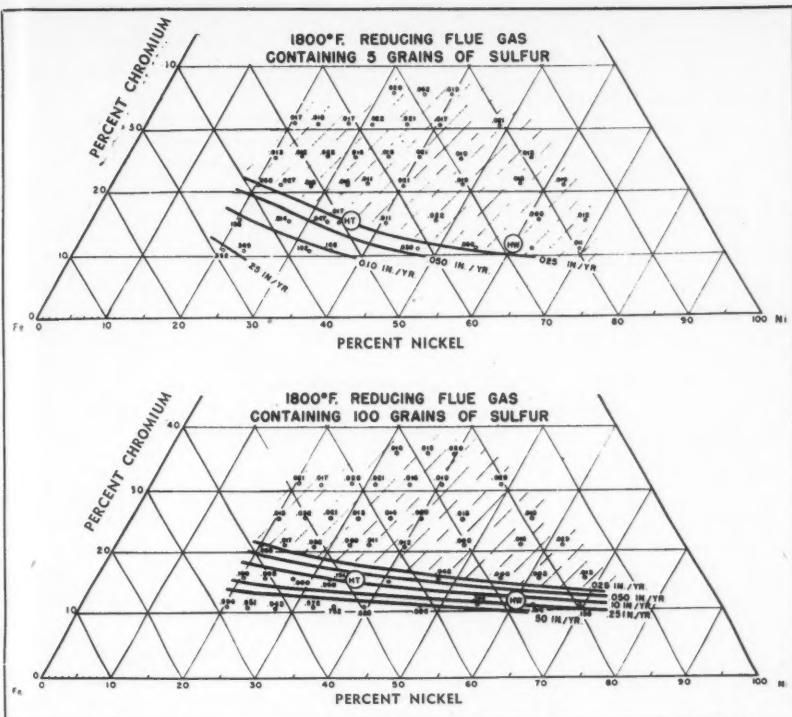
Figure 16—Influence of alloy content on extent of corrosion penetration per year as indicated by 100-hour tests at 1800° F. in reducing flue gas containing sulfur. Alloys also contain 0.4 percent C, 1.25 percent Si, 0.75 percent Mn. (Alloy Casting Institute: Reference 14.)

level. Comparing the amount of corrosion obtained for the HT group of alloys with that for the HH alloys shows that about the same order of corrosion resistance is obtained under this flue-gas exposure condition with alloys of 35% Ni-16% Cr as is obtained for the alloys of about 26% Cr-12% Ni.

An extensive systematic study of the influence of alloy composition variations of Fe-Ni-Cr alloys, on the corrosion resistance in oxidizing and reducing flue gases is being sponsored by ACI at Battelle Memorial Institute. While the work is not yet completed, a preliminary report of the results has been made in the Alloy Casting Bulletin.[14]

Figures 15 and 16 present certain of this published information showing the composition limits for certain intensities of corrosion for alloys in the range of 11 to 36 percent chromium and 20 to 69 percent nickel. The exposure temperature is 1800° F., the time of exposure 100 hours. The flue gases represent the so-called oxidizing and reducing combustion conditions and contain

SIMPLIFIED FLOW CHART OF CORROSION APPARATUS
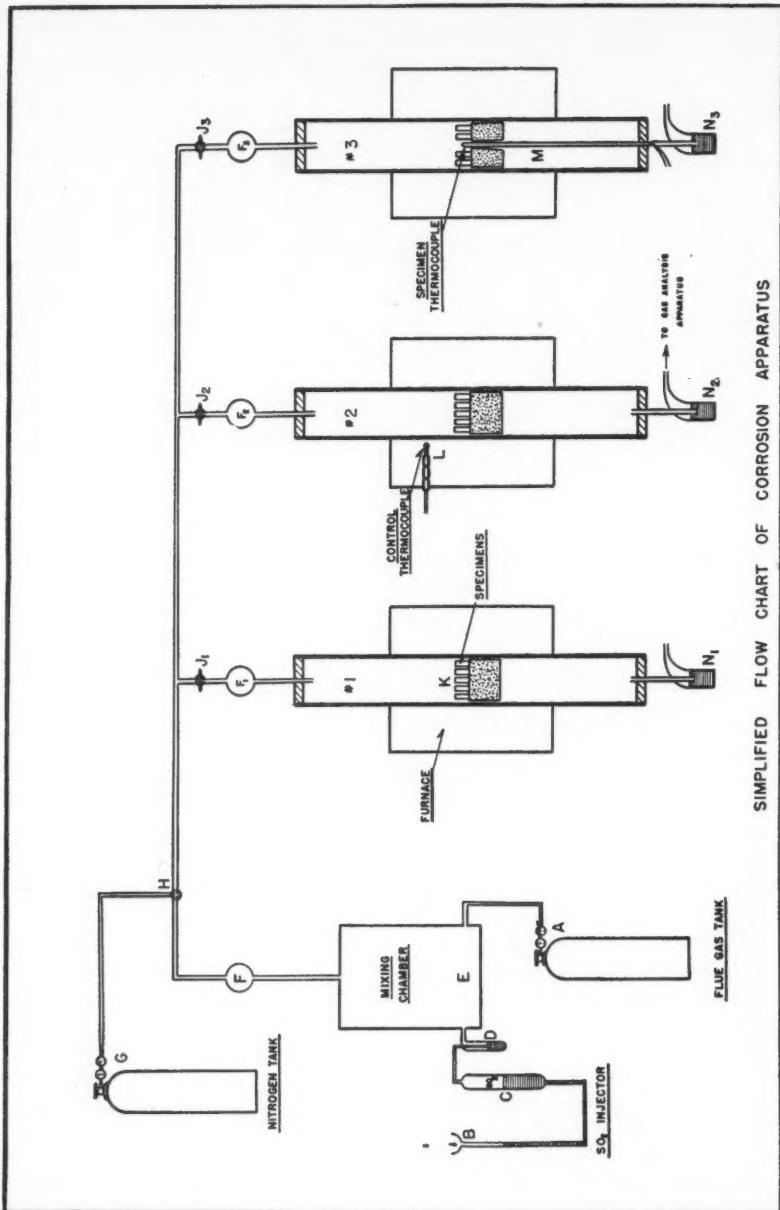
Figure 17

sulfur contents of 5 and 100 grains per 100 cubic feet of gas.

By making a comparison of the position of the isocorrosion contour lines obtained for the oxidizing flue gases, it is apparent that, by increasing the sulfur content from 5 grains to 100 grains, the flue-gas atmosphere becomes mildly more corrosive. The minimum chromium contents and/or nickel contents for maximum corrosion resistance are indicated to be raised moderately when the ambient atmosphere contains 100 gS.

The reducing flue gas with 5 grains of sulfur is shown to be less corrosive than the oxidizing flue gas of this same sulfur content, in the case of those alloys containing less than 15 percent chromium and covering the whole range of nickel contents. When the sulfur content of this reducing atmosphere is increased to 100 gS, however, the corrosion becomes intense for all alloys with less than 16 percent chromium, and is most severe for alloys with only 11 percent chromium over the whole range of nickel contents. It is, however, indicated that trouble from this sulfur content can be avoided even in the highest nickel content alloys by simply increasing the chromium content of the alloy.

It is to be realized that these 100-hour corrosion tests are not comprehensive enough to fully evaluate the alloys and that, at their best, they only show the range of alloy compositions definitely of no merit and indicate the range of compositions which are of interest for further critical study. Further weeding of unsuitable alloys requires testing at other, and preferably higher, temperatures and for longer periods of time.

It is considered in our work at Battelle Memorial Institute that, for those alloys indicated to be of possible merit in the short-time tests, long-time tests must be conducted to obtain a more complete evaluation of the extent of superiority of one alloy over another. The influence of alternate heating and cooling, and in addition, mechanical shock, must be studied to make a final selection of the most suitable alloy for use under service conditions. Such work is in progress at the present time for this same series of alloys reported on in Figures 15 and 16.

The gas atmosphere being used in these flue-gas corrosion studies is prepared by taking the commercial cylinders of the desired gases such as carbon dioxide, carbon monoxide, oxygen and nitrogen and bleeding measured quantities into a gas house in which they are mixed and then pumped into high-pressure cylinders. To obtain the water vapor wanted in the furnace atmosphere, hydrogen and oxygen in the required amounts are included in the mixed tank gas, and their combination in the heated furnace chamber provides the water vapor.

As shown in Figure 17, the gas is introduced at a controlled rate into a mixing chamber (E), into which the desired quantity of sulfur dioxide is also continuously being introduced from the sulfur dioxide injector. The total gas flow is measured at F. Pressure-head adjustments, by means of the mercury heads, N_1, N_2, and N_3, divide the gas equally among the furnaces. The

Figure 18—Sectioned view of furnace tube at furnace center, showing arrangement of specimens, fused silica thermocouple tube, and refractory (K-30) specimen holder. (Alloy Casting Institute: Reference 20.)
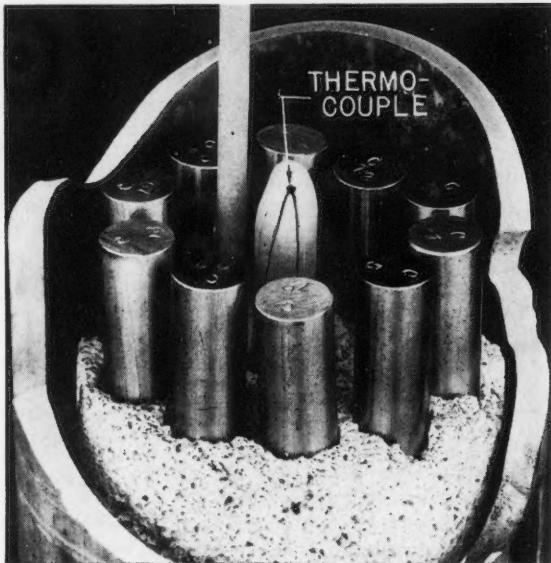
analysis of the inlet gas may be determined by withdrawing a sample at H, and the exit gas is sampled at N at regular intervals. The composition of the gas discharging from the furnace is assumed to be that contacting the specimens. The surface metal loss by corrosion is calculated from change in weight measurements upon removal of the surface corrosion product. The descaling is accomplished cathodically in a molten caustic salt bath (60 percent sodium hydroxide, 40 percent sodium carbonate),[15] using a current density of 400 amperes per square foot for a period of one to four minutes, depending on the nature of the scale.

In conducting the exposure, the weighted samples held on a refractory holder, as shown in Figure 18, are inserted into the furnace. The apparatus is sealed and checked for pressure tightness.

Nitrogen is then introduced into the system to displace the air, and the furnaces are heated to the exposure temperature. When the required temperature is reached, the nitrogen is shut off, and the flue gas introduced continuously at a controlled rate. At the end of the desired exposure time, the flue gas is shut off and nitrogen again introduced, and the specimens are allowed to cool to room temperature. Figure 19 shows the appearance of one group of specimens of different compositions on removal from the furnace.

Determining the extent of corrosion by descaling the corroded specimens and determining the weight of metal loss is thought to be a more accurate method than the often-used weight-gain measurements. The weight-loss method has the advantage of allowing a direct conversion
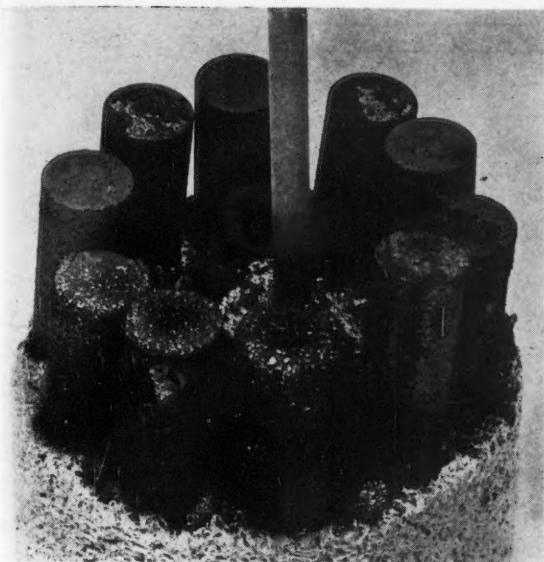
Figure 19 — Appearance of specimens upon removal from furnace tube after 100-hour exposure to a sulfur-containing reducing flue gas at 1800° F. (Alloy Casting Institute: Reference 20.)

to a depth of metal lost by corrosion scaling or, in other words, the depth of penetration of the surface corrosion. To convert a gain-in-weight measurement to a depth of penetration, an assumption must be made of the composition of the scale. Also, the test must be conducted in a manner to allow collecting any scale which flakes off on cooling, which is almost an impossiblity when more than one specimen is being tested. Even this technique does not account for scale lost in the furnace. Evidently, by the gain-in-weight technique it is only necessary to have the loss in weight by flaking of scale equal to the gain in weight by scale formation to have what might be reported as a super alloy.

Subsurface Corrosion

When concerned with air and flue-gas corrosion, attention must be given to learning whether the alloys are prone to such types of subsurface damage as decarburization and intergranular and/or interdendritic oxidation penetration in addition to the general surface scaling. Such information is obtainable by metallographic studies. Information on these points in the literature is meager.

Figure 20, from the studies of Brasunas, Gow, and Harder,[11] shows the region of Fe-Ni-Cr alloy compositions in which various forms of subsurface corrosion attack have been observed by microscopic study of transverse sections of specimens that had been exposed for 100 hours at 1800° F. in an air atmosphere.

Figures 21 and 22 illustrate the different types of subsurface attack observed. All such forms of subsurface corrosion attack undoubtedly have some damaging influence on
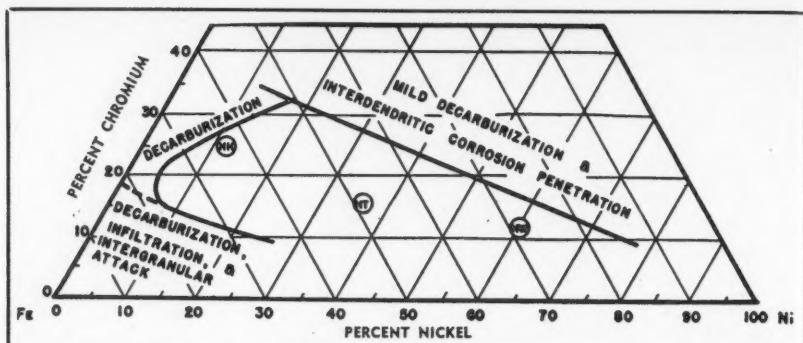
Figure 20—Types of subsurface corrosion attack found in various alloy regions in air atmosphere at 1800° F. for 100 hours. The region of alloy compositions in which substantially no subsurface corrosion attack was evident includes the three commercially important alloy types, HH (25 percent Cr—12 percent Ni), HT (35 percent Ni—16 percent Cr), and HW (60 percent Ni—12 percent Cr). In general, as the composition departs from the region of substantially no subsurface attack, the intensity of attack was found to increase. (Brasunas, Gow and Harder: Reference 11.)

the strength properties. Oxide penetration would provide a notch effect to accelerate failure under tensile stresses, shock, or alternate thermal stresses. Also, the alloys are known to have maximum creep resistance at an optimum carbon content, and decarburization would be expected to lower the resistance of the alloys' flow (creep) under stress. Under certain conditions of stressing, it is, however, probable that the increased plasticity of a decarburized surface layer may be a benefit rather than a detriment.

General Discussion of Corrosion Scaling

Numerous investigators have proposed theories for the mechanism of corrosion scaling, and the subject is quite controversial. Certain experimental facts to be taken into account will be briefly mentioned.

The quantitative metal-loss data presented in this paper show that the corrosion behavior to be expected of an alloy cannot be generally predicted from the known corrosion behavior of component elements, and the proportions of these elements in the alloy. It has been shown that the stability of Fe-Ni-Cr alloys against oxidation corrosion increases with increasing chromium contents up to an optimum amount of chromium at a constant nickel content, or increases with increasing nickel contents up to an optimum amount of nickel, at a constant chromium content. In other words, the optimum nickel or chromium content for maximum corrosion resistance varies as the nickel or chromium levels being considered are altered. Also, the optimum amounts of nickel and chromium vary with the temperature being considered.

It has been shown that certain alloys change rather abruptly over a small temperature range from having satisfactory to unsatisfactory corrosion resistance.

Elements such as cobalt, tungsten,

and molybdenum, which have relatively poor oxidation resistance, have been shown not to be detrimental or are indicated to enhance the oxidation scaling resistance when present in certain amounts in certain Fe-Ni-Cr alloy compositions. While it has not been discussed in this paper, it is claimed that small additions of such metals as calcium, thorium, and cerium improve markedly the scaling resistance of nickel-base alloys out of all proportion to the amount of added element.

Studies of numerous investigators[16,17,18] of the chemical and physical character of the oxide scale layer have shown that they are not homogeneous but that there is a preferential distribution or considerable stratification of the elements of the alloy in the scale. Since the degree of corrosion is definitely not a direct function of the rates of corrosion of the constituent elements, the indications are that the tendency for stratification of the elements in the corrosion product causes certain of the elements to become segregated in a manner to provide a layer of complex metal oxides which hinders the progression of corrosion to a greater extent than possible by any of the single metal oxides. It is likely that, for the whole range of Fe-Ni-Cr alloys, the protective layer contains a substantial amount of chromium oxide.

It has been suggested by Mott,[19] in theorizing on the mechanism of the formation of protective oxide films, that initially a mixed oxide is formed with the various metals present in the oxide in the same ratio as in the alloy, but as the film thickens some segregation of the oxides occurs as a result of the different rates of diffusion of the elements in the alloys through the oxide layer to react with the oxygen at the oxide-oxygen interface. It is believed that oxygen ions, molecules, or atoms cannot diffuse *interstitially* through the oxide layer, owing to their larger size.

Two processes of diffusion of metallic ions in the oxide are considered. One is that of metallic ions leaving the surface of the metal and moving in the oxide from one interstitial position to another until they reach the oxide-oxygen interface. The concentration of metal ions will decrease toward zero as the oxide-gas interface is approached, and the concentration gradient thus established will lead to a flow of metal ions. For a given concentration gradient, the ease with which the ion diffuses through the lattice will depend on its ionic size.

A second process considered likely to occur at the same time in the case of mixed oxides is that of a trivalent metal ion, such as chromium and aluminum, in an interstitial position changing places with a divalent ferrous ion in the oxide lattice. It is also considered likely that differences in the rates of diffusion of the various atom species within the metal are a factor and that the metals can occur in the scale in different proportions than in the metal. It is postulated that, by such processes, the stratification of the oxides occurs on an alloy to provide a layer of a particular lattice through which the diffusion of new metal ions is hindered.

The essential requirement for a scale layer to give protection under
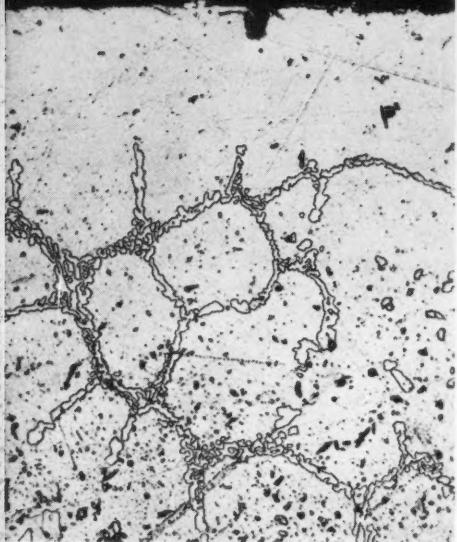
A. Alloy C-85, 26% Cr—0.0% Ni.
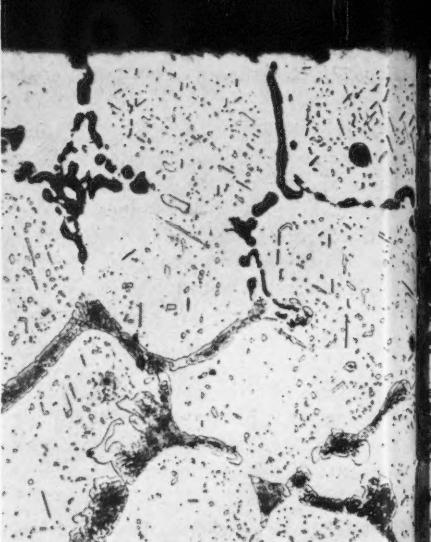
B. Alloy C-55, 31% Cr—36% Ni.
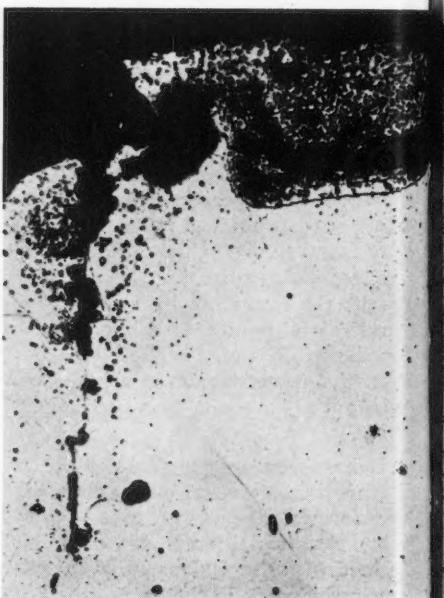
C. Alloy C-1, 11% Cr—20% Ni.

Figure 21—Various forms of subsurface corrosion occurring with some Fe-Ni-Cr alloys upon exposure to air atmosphere at 1800° F. Etched in aqua regia. Mag. 250X. Note: A—Zone of intense decarburization. B—Oxide penetration progressing inward along the primary eutectic carbides. C—The area of mixed metal and oxide particles, also the progression of intergranular corrosion. (Brasunas, Gow and Harder: Reference 11.)
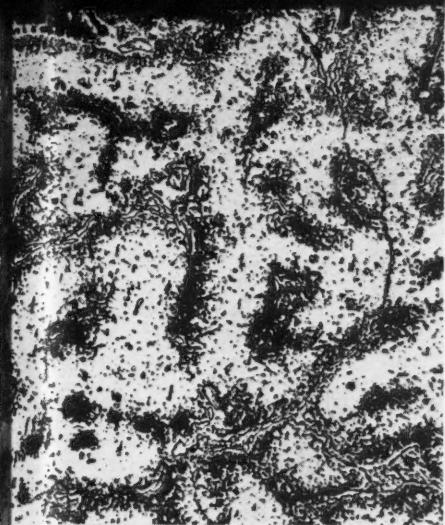
A. Alloy C-26, Regular HH Alloy
25% Cr—12% Ni.
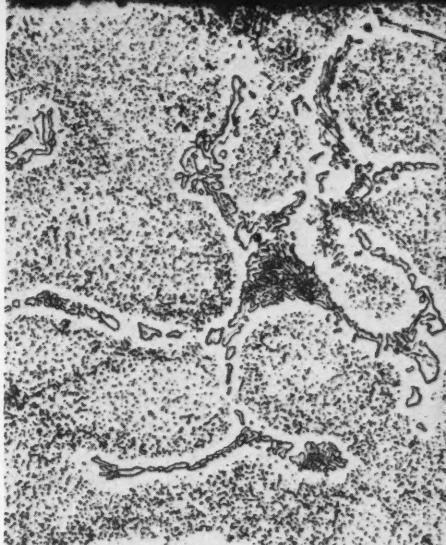
B. Alloy C-22, Regular HT Alloy
16% Cr—36% Ni.
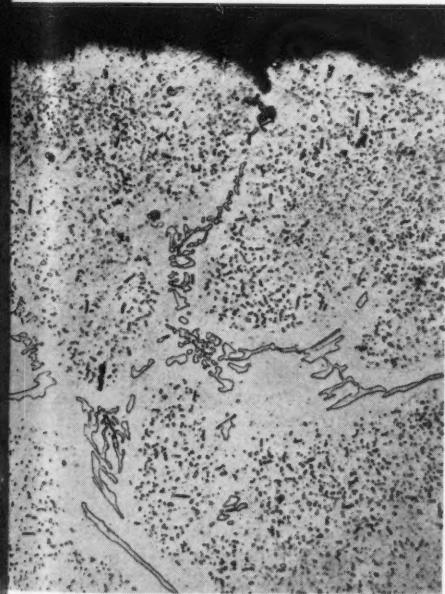
C. Alloy C-10. This alloy closely resembles
an HW type, 11% Cr—68% Ni.

Figure 22—Subsurface corrosion of some commercial Fe-Ni-Cr alloys exposed in an air atmosphere at 1800° F. for 100 hours. Etched in aqua regia. Mag. 25X. Note very slight extent of decarburization and interdendritic corrosion on these commercial type alloys. (Brasunas, Gow and Harder: Reference 11.)

service conditions is, of course, that the layer offering the protection be solid and adherent under the action of alternate heating and cooling and mechanical shock. It is not known whether the protective oxide layers formed on a wide range of Fe-Ni-Cr alloys at one temperature and hindering the rate of corrosion to about the same degree as measured in a short-time test are of different compositions. At least the proportions of the different metal ions tending to diffuse through the scale vary.

In any diffusion process, temperature is an important factor, and this in itself may be sufficient to account for the increased corrosion at increasing temperatures. In cases of an abrupt change in corrosion resistance within a narrow range of temperatures, it is probable that composition changes occur in the protective oxide to change its structure and hence the degree of protection it offers. However, it is also probable that the effect of temperature on the diffusion rate of the different ion species is enough different that it is to be expected that the proportions of the various alloying elements present in different alloys will have some effect on the maximum temperature at which the protective barrier seems to break down in a manner that an alloy changes rather abruptly from having satisfactory to unsatisfactory corrosion resistance.

It is evident that too little is known about the protective coatings which form on heat-resistant alloys and that that subject requires intensive study along with the composition of the alloys.

Summary

This survey of hot-gas corrosion has attempted to accomplish three broad objectives, which are as follows:

1) To show within what limits of nickel and chromium contents alloys with the most useful heat-resistant qualities are found.

2) To bring out the fact that gas-atmosphere corrosion is definitely complex, and that the fundamentals are inadequately understood at the present time. This emphasizes the need for caution in making or accepting broad generalizations regarding the relative corrosion resistance of different heat-resisting alloys.

3) To stress the procedures considered desirable for conducting laboratory lists, with the thought that such informations might lead eventually to a standardization of test methods.

Acknowledgment

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DISCUSSION

*By E. F. Wilson**

The contribution of Mr. Gow is particularly appropriate where the effects of surface damage of metals by chemical attack are to be considered. While a considerable amount of attention by engineers has been paid to the effect of aqueous media, there has been a much less systematic approach in the use of standardized techniques where high-temperature, gas-phase attack has been investigated. In the studies conducted by Mr. Gow and his associates under the sponsorship of the Alloy Casting Institute, particular consideration

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has been given to careful and reproducible experimental methods. With the establishment of some fundamental aspects of the problem, more comprehensive investigations can be conducted, and correct interpretations made possible.

In illustrating the effect of chemical composition on phase stability and correspondingly on the creep and rupture strengths, Mr. Gow has selected alloys well qualified to tolerate the temperature conditions and test environment. Had the selection been less favorable, the fracture time lines in Figures 4 and 5 might have shown a break at some time

period and the establishment of a new trend line with a more rapid decline of stress to rupture for continued exposure. Such breaks are often attributable to impairment of the mechanical properties by oxidation or other surface deterioration. These deviations serve to point out the need for materials which can consistently maintain good mechanical properties in their service surroundings.

The complexity of gas-atmosphere corrosion has been pointed out by Mr. Gow together with some of the factors which contribute to this complexity. It might also be stressed that in a mixture of gases, the integral effect cannot be always surmised on an additive basis from studies of the individual gases. Furthermore, their associate effects will be found to vary with temperature. It is quite possible that apparent anomalies may be concerned with momentary thermal dissociation of a non-equilibrium character which increases the instantaneous activity (or fugacity) to an unusual extent. Certain it is that attempts to reproduce atmospheres specific to a definite process or industrial installation are not always successful.

Were it not for the chemical inertness and thermal insulating value of many metal oxide scales, the metals themselves would not last long with high-temperature exposure. For example, where subjected to only a moderately abrasive action of dust or fine ash, it has been found that scale on some alloy steels may be removed to the extent that progressive oxidation and severe metal wastage results. Proper design, to baffle or decrease the velocity of thermal gas currents, may correct this condition. Where this is impossible, consideration must be given to scale adherency and the selection of an alloy composition which assures a satisfactory adherence.

Selective attack on specific phase constituents on their discontinuities is a feature pointed out by Gow in illustrating sub-scale attack. The severity of some types of sulphur attack is attributable to this effect. However, a minor vulnerability to non-uniform penetrative attack does not necessarily imply inapplicability for many service requirements. Irregular, but fully distributed micro-scale notch effects under static loading need not be serious, whereas a highly localized or single penetrating notch can result in premature failure.

In the work reported by Mr. Gow, temperatures not in excess of 2200° F. have been employed. Due to difficulties of control, or design considerations, temperatures beyond such tolerable maxima will sometimes be encountered, occasionally for only brief intervals. The performance of commercial alloys under these conditions cannot be extrapolated from test results conducted at not over 2200° F. Often there will be experienced formation of highly reactive liquid phases, with their fusion temperatures lowered by diffusion segregation. Unbalanced gas conditions and highly fluctuating combustion reactions frequently are found in the higher temperature regions of furnaces. Temperature changes are similarly erratic with pronounced thermal shock effects.

Where extraordinary high temperature conditions occur, the design or operating engineer will sometimes

fail to recognize this severity and request new or unusual alloys to meet these conditions. Often these are not technologically available. A process of education would be helpful to express the need for improved installation design with protective features such as relocation of alloy parts to good advantage, use of cooling fins, access and extension of surfaces to normal air cooling and other alleviating features to improve the service life of the alloy parts.

The intelligence which the National Association of Corrosion Engineers will further, should contribute much to better understanding between the user and the manufacturer of alloys for high temperatures and resistance to hot-gas attack.

Author's Closure

I wish to thank Mr. Wilson for the discussion which he prepared. This discussion serves to stress the need for selecting materials for high temperature engineering applications which assure satisfactory stability in the ambient atmosphere in which it is to operate in order to maintain the alloys' inherent mechanical properties.

He has also stressed the need for giving strict attention to design features, to avoid localized overheating to temperatures not considered in the engineering design. The importance of this can be readily understood, because both load carrying ability and the severity of corrosion are a function of temperature.

Arsenic as a Corrosion Inhibitor
In Sulfuric Acid*

By A. Wachter*, R. S. Treseder* and M. K. Weber*

THAT ORGANIC arsenic compounds behave as inhibitors for the corrosion of steel by sulfuric acid was reported as far back as about 100 years ago.[1] Since then there have been numerous investigations[2, 3, 4, 5, 6] of various phases of this behavior, the emphasis being placed on inhibition of relatively dilute sulfuric acid. For example, it has been reported[4] that the corrosion rate of carbon steel in 0.5 normal sulfuric acid (2.4 percent H_2SO_4) at room temperature was reduced 98 percent by addition of 0.05 percent arsenious oxide to the acid.

The generally accepted mechanism for the corrosion inhibiting action of arsenic compounds in sulfuric acid solutions is that deposition of an adherent film of metallic arsenic occurs on the cathode areas which stifles the normal cathode reaction involving discharge of hydrogen ions owing to the high hydrogen overvoltage of arsenic.[4]

Heretofore, the principal practical application proposed for arsenic compounds as corrosion inhibitors has been in acid baths for pickling of steel. This application is not common now owing to several disadvantages

of the arsenic compounds as compared to the better organic inhibitors now available. These disadvantages include: (1) safety hazards resulting from handling the inhibitor and from the arsine produced during pickling operations, (2) tendency to promote hydrogen retention in steel, even to the extent of blistering the steel, (3) deposition of arsenic coatings which have been reported as hindering subsequent finishing operations, and (4) occasional occurrence of pitting.

This paper is concerned primarily with the inhibitive properties of arsenic compounds in strong sulfuric acid solutions, i.e., higher than 50 percent concentration, such as are used in several petroleum processes. The hot acid polymerization processes employ 63 to 72 percent sulfuric acid at 75 to 100° C. to polymerize butylenes to gasoline range polymer. In another process, 60 to 70 percent sulfuric acid at 20 to 40° C. is employed for extraction of isobutylene from a mixture of butanes and butylenes, followed by polymerization at temperatures up to 100° C. Sulfuric acid at higher concentrations is often employed in alkylation processes, 88 percent acid at about 40° C. being used to alkylate benzene with propylene to give cumene, and
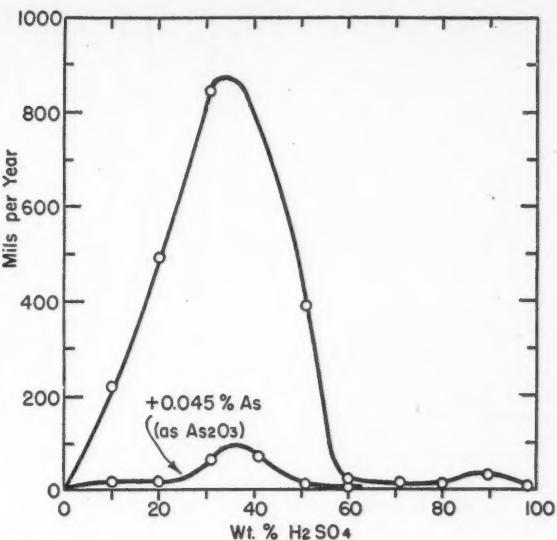
Figure 1—Corrosion of carbon steel by sulfuric acid at 24° C. Conditions: Low-carbon (0.06C) cold-rolled steel immersed eight days in 400 ml. of H₂SO₄ (technical), with and without added arsenic (as As₂O₃), stagnant, at room temperature (approximately 24° C.) air atmosphere. Corrosion rates from weight losses.

98 to 100 percent sulfuric acid at 0-10° C. being used to alkylate butylenes with isobutane.

In some of these processes, use of sulfuric acid has resulted in severe corrosion of carbon steel. Since substitution of a resistant material of construction would be rather costly, the possibility of using a corrosion inhibitor to protect the steel appeared attractive. Subsequent research showed arsenic compounds to be most generally suited for this purpose. Data were obtained that show the corrosion characteristics of strong sulfuric acid and the inhibitive effect of arsenic compounds over a wide range of temperature and acid concentration conditions. Several sets of conditions were emphasized owing to their connection with particular process corrosion problems.

Corrosion of carbon steel by sulfuric acid varies considerably as a function of the acid concentration, and is affected markedly also by many other factors. It is informative to review the main features of these effects before enlarging on inhibition with arsenic in limited ranges of use conditions. It is well known that sulfuric acid is highly corrosive to steel at room temperature even under stagnant conditions in the concentration range up to about 55 to 60 percent weight H_2SO_4, that maximum corrosiveness is found with about 35 percent H_2SO_4, and that only relatively slight corrosion occurs with about 60 to 100 percent H_2SO_4. These relative effects are shown graphically in Figure 1.

The decrease in corrosiveness in the higher concentration range may be attributed not only to reduced hydrogen ion activity but also to the very low solubility of the ferrous sulfate corrosion product in
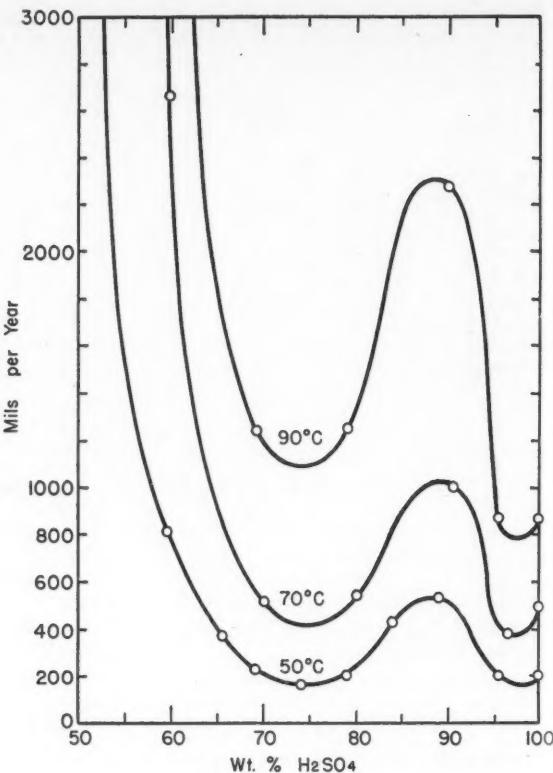
Figure 2—Corrosion of carbon steel by hot, strong sulfuric acid. Conditions: Cold-rolled carbon steel ribbon in stirred H_2SO_4. Corrosion rates from changes in electrical resistance of ribbon in exposures of about one hour.

strong sulfuric acid. The marked effect of arsenic trioxide in reducing the corrosiveness of 0.0 to 55 percent H_2SO_4 is also shown in Figure 1.

An enlarged view of relative corrosion effects in the range from 50 to 100 percent H_2SO_4 and of the influence of temperature is shown graphically in Figure 2. It is interesting to note the occurrence of another maximum in corrosiveness at about 88 percent H_2SO_4, and the marked corrosion accelerating effect of increasing temperature, especially in the region of 88 percent H_2SO_4. The relative effect of arsenic in in-

hibiting corrosion by these stronger acid solutions at an elevated temperature is shown in Figure 3. It is seen that the arsenic at a concentration of 0.076 percent is not nearly as efficient or effective in the region around 88 percent H_2SO_4 as it is in 60-70 percent H_2SO_4.

Presumably any soluble trivalent arsenic compound may be used to inhibit sulfuric acid. The only compounds used in this research were arsenic trioxide (As_2O_3) and sodium meta-arsenite ($NaAsO_2$). The latter was the preferred form in spite of its lower content of arsenic because
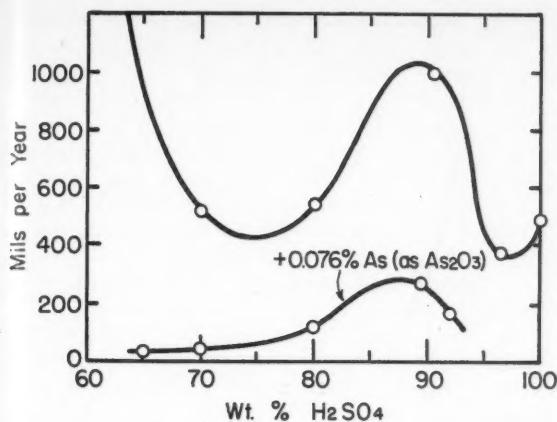
Figure 3—Arsenic as a corrosion inhibitor for carbon steel in sulfuric acid at 70° C. Conditions: Cold-rolled carbon steel ribbon in stirred H_2SO_4 at 70° C. Corrosion rates from changes in electrical resistance of ribbon in exposures of about one hour.

it is readily available commercially as a concentrated solution in water, and because powdered arsenic trioxide dissolves very slowly and with great difficulty in acid or in water. Up to about 0.5 percent $NaAsO_2$ could be dissolved in 50 to 65 percent H_2SO_4. One way in which this was done was by addition of a 50 percent solution of $NaAsO_2$ in water to 98 percent H_2SO_4 with mild agitation, followed by dilution with water to the desired strength.

The influence of arsenic concentration and its effectiveness in a hot 72 percent acid which had been used
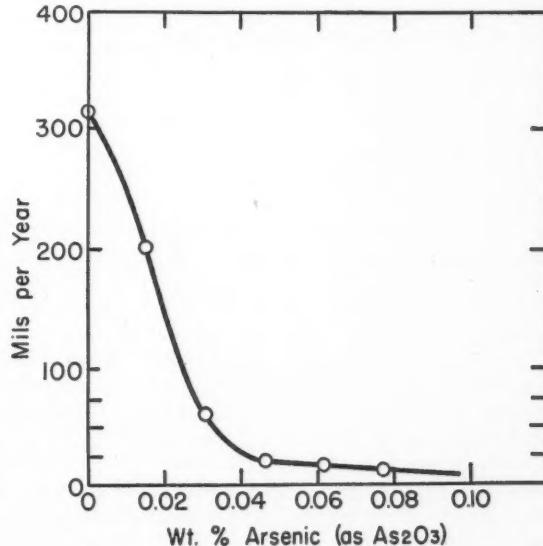
Figure 4—Inhibition by arsenic of plant used 72 percent sulfuric acid. Conditions: Cold-rolled carbon steel ribbon in stirred 72 percent H_2SO_4 at 76° C. Corrosion rates from changes in electrical resistance of ribbon in exposures of about one hour.
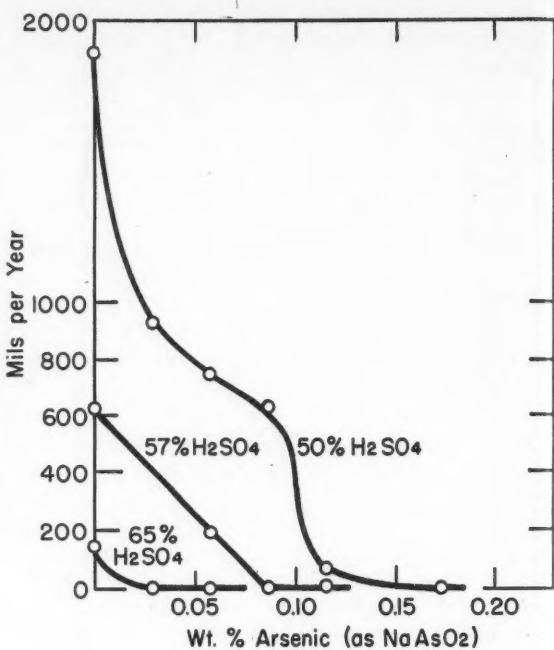
Figure 5—Effect of arsenic concentration on corrosion of carbon steel by sulfuric acid at 49° C. Conditions: Two strips of carbon steel (0.22 C., class A tank plate), each 0.75 inch by 3 inches, immersed as baffles in 600 ml. of H_2SO_4 (technical-grade) containing various concentrations of $NaAsO_2$. Acid stirred with 0.5 inch by 2-inch steel strip rotated in its flat plane with peripheral velocity of 12 to 14 feet per second. Air atmosphere. Duration 1 to 15 days. Corrosion rates from weight losses.

for polymerization of butylenes is shown in Figure 4. This is noteworthy because the acid was contaminated with hydrocarbons and their reaction products with the acid. It is seen that relatively low corrosiveness was attained with 0.05 percent or more arsenic.

A fairly extensive series of experiments was made to determine the limiting conditions of usefulness of arsenic for inhibiting corrosion of steel by hot 50-65 percent H_2SO_4. The acid concentrations studied were 50, 57, and 65 percent technical grade sulfuric acid, at 49 and 85° C., with different concentrations of arsenic added in the form of sodium metaarsenite. The steel used in most of the experiments was 0.22 carbon Class A tank plate, strips of which

were machine-milled smooth and then surfaces ground on an emery wheel. The acid in each experiment was vigorously stirred with a weighed and calipered-measured flat strip specimen rotated at high velocity in its flat plane. The experiments, in general, were run from 1 to 15 days, the longer times being employed when corrosion losses were low. The atmosphere over the acid was air, since experience[7] has shown that oxygen does not affect significantly the corrosion of steel by sulfuric acid above 50 percent concentration.

Results at 49° C. with the fixed strip specimens are summarized graphically in Figure 5, all corrosion rates having been calculated from weight losses. Attack on these specimens was uniform and general,

without pitting. It is seen that arsenic was able to reduce corrosive attack to relatively trivial values (1 to 5 mils per year) under these conditions. It is interesting to note that greater concentrations of arsenic were required for complete suppression of attack in the more dilute acids.

Several experiments with different concentrations of arsenic were made in 57 percent H_2SO_4 with specimens of SAE 1020 and 1040 steels, a 0.06 carbon steel, and seamless carbon steel pipe. Corrosion rates for all of these were of the same magnitude as for the tank plate steel. A special pair of experiments showed that the inhibitor also is effective, particularly under high velocity conditions, in the acid emulsified with hydrocarbon (diisobutylene).

Confirmation of Effectiveness Obtained

Confirmation was obtained of the effectiveness also of arsenic in 65 percent acid which had been used in an isobutylene polymerization plant, and which contained about six percent dissolved or reacted hydrocarbons. In laboratory experiments with specimens from ¾-inch seamless steel tubing (ASTM specification No. A-179-37) at 49° C. in acid containing 0.13 percent arsenic for 1 day, the following results were obtained:

Acid	Corrosion Rate Mils/Yr.
Plant used 65% H_2SO_4	3, 6
Fresh 65% H_2SO_4	2, 9
Plant used 65% H_2SO_4 saturated with SO_2	3
Fresh 65% H_2SO_4 saturated with SO_2	9

It is interesting to note that bubbling sulfur dioxide continuously through the acid did not have any detectable influence on results.

In order to determine whether inhibition with arsenic of acid used in polymerization processes would result in arsenic being found in the polymer, a butylene polymerization experiment was made with 71 percent H_2SO_4 containing 0.2 percent As_2O_3 at 76° C. Analysis of the crude polymer showed that it contained 0.004 percent As. When this polymer was washed three times with equal volumes of 10 percent sodium hydroxide (NaOH) solution at room temperature, the arsenic content was reduced to 0.0002 percent As. Refluxing the crude polymer for one hour with 2 volumes of 10 percent NaOH solution reduced the arsenic content to 0.0001 percent As. No arsenic could be detected in the total dimer fraction boiling up to 134° C. obtained by distillation of the unhydrolyzed crude polymer. In view of these results it seems clear that the usual processing steps following polymerization would tend to remove completely the traces of arsenic extracted from acid by the crude polymer.

Reduces Attack at High Peripheral Velocities

It was found, from examination of the stirrer specimens used in each experiment, that arsenic also was able to effectively prevent attack (corrosion rates of 2 to 10 mils per year) at the high peripheral velocities of 12 to 14 feet per second. Protection under these conditions was observed only when sufficient arsenic was present to reduce attack to negligible values on the fixed specimens. These results under high velocity conditions appear reasonable in view of the formation of a hard, tenacious
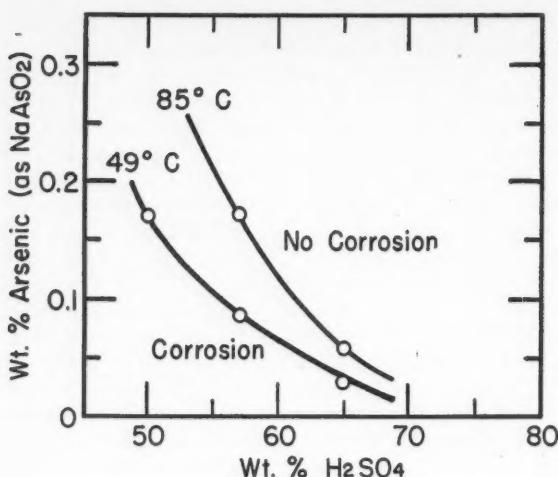
Figure 6—Minimum concentration of arsenic for inhibition of corrosion of steel by sulfuric acid.

deposit of metallic arsenic on the steel. With no inhibitor present, or with less than inhibiting concentrations, attack on the leading edges of the rotated strips reached colossal corrosion rates of 10 to 30 inches per year as indicated by change in strip dimensions.

On the basis of the curves in Figure 5, it is possible to derive a curve, Figure 6, that shows the minimum concentrations of arsenic in various strengths of acid to achieve substantially complete protection of carbon steel under the experimental conditions. This curve serves as a boundary for two concentration areas, in one of which corrosion occurs, and in the other no corrosion occurs.

A boundary curve for the higher temperature condition of 85° C. is also given in Figure 6, but this curve was derived from less extensive data than were obtained at 49° C. These curves show that the concentration of arsenic needed to suppress corrosion increases markedly in hot acids

as the concentration of acid is reduced, and indicate that as temperature is raised, increasingly greater arsenic concentrations are required. It should be understood that minimum inhibiting concentrations are usually quite sensitive to many exposure conditions, and curves of this type may be used for practical applications only as a rough guide.

It was found that the presence of copper dissolved in the acid is an adverse factor which tends to vitiate the effectiveness of arsenic as an inhibitor. Even very low concentrations of copper (as $CuSO_4$) had a marked effect. For example, with carbon steel in 57% H_2SO_4 at 49° C. in 1-day experiments, the following comparative data were obtained:

Additions to 57% H_2SO_4	Corrosion Rate Mils/Yr.
0.1% $NaAsO_2$	5
0.1% $NaAsO_2$ + 0.001% Cu	69
0.1% $NaAsO_2$ + 0.01% Cu	470
0.2% $NaAsO_2$	3
0.2% $NaAsO_2$ + 0.01% Cu	67

Figure 7—Influence of cupric ion on inhibition of 57 percent sulfuric acid by arsenic. Conditions: 0.22 carbon steel strips, 0.75 by 3 inches, in stirred 275 ml. of 57 percent H₂SO₄ (technical), at 49° C., for 24 hours. Air atmosphere. One series with different concentrations of arsenic (as NaAsO₂) added to the acid, and a duplicate series with arsenic and copper (as CuSO₄) added. Corrosion rates from weight losses.
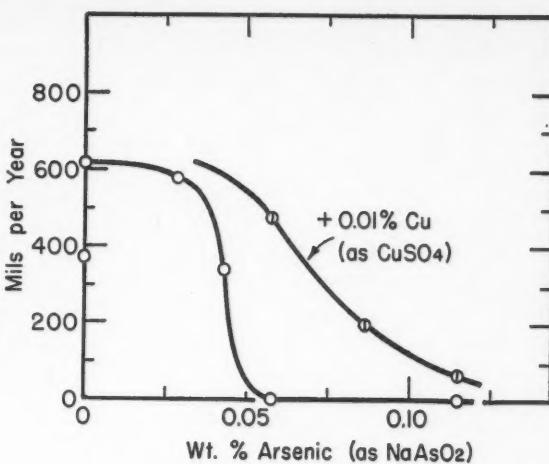
Additional data are given graphically in Figure 7, showing that the presence of 0.01 percent copper increases the inhibitor requirements considerably. It may be presumed that copper plates out with the arsenic and thus impairs polarization by the arsenic at cathodic areas on the steel, since it was found that copper deposited on steel in hot 57 percent acid containing 0.01 percent Cu as CuSO₄, and that arsenic deposited on a copper strip immersed in acid containing 0.1 percent NaAsO₂.

It was mentioned earlier that arsenic did not appear as effective in acid strengths around 88 percent H_2SO_4 as at lower concentrations. Further experiments with hot 88 percent acid confirmed that insufficient benefit is derived under strongly agitated conditions from addition of reasonably small percentages of arsenic to this acid concentration. A portion of the results obtained are summarized in Table I, showing relatively poor efficiency of inhibition. The corrosion rate values quoted should not be taken too literally, inasmuch as most experiments with 88 percent H_2SO_4 were characterized by large uncertainty in values of corrosion losses.

It is interesting to examine the effect of arsenic in hot strong sulfuric acid on corrosion of several nonferrous metals. This is particularly

TABLE I

Effect of Arsenic in 88% Sulfuric Acid

Conditions: Polished carbon steel strips, each 0.25 by 2 inches, in 1500 ml. 88% sulfuric acid (c.p.) saturated with FeSO₄, for 2 days. Air atmosphere. One strip rotated in its flat plane with peripheral velocity of 15 ft./sec. Corrosion rates from weight losses.

TEMP., °C.	Arsenic Added, Wt. Percent	Corrosion Rate, mils/yr.	
		Stationary Specimen	Stirrer Specimen*
40	0	30	350
	0.1	30	70
	0.2	20	30
	0.5	30	30
90	0	400	1700
	0.1	130	230
	0.2	100	270

* Marked localized attack on the leading edges of rotated specimens at rates of 2,000 to 11,000 mils/yr., with or without arsenic.

TABLE II
Effect of Arsenic on Corrosion on Non-Ferrous Alloys by Sulfuric Acid

Conditions: Polished duplicate strips, each 0.75 by 3 inches, in stirred technical grade acid. Air atmosphere. Corrosion rates from weight losses (no pitting detected).

METAL	Wt. % H_2SO_4	Temp. °C.	Hours	Wt. % As (as As_2O_3)	Corr. Rate. mils/yr.
Chem. Lead...	71	76	24	0	10
"	"	"	"	0.076	14
"	86	182	8	0	1020
"	"	"	"	0.076	960
"	93	221	6	0	4150
"	"	"	"	0.076	3820
Admiralty Brass......	71	76	24	0	27
"	"	"	"	0.076	27
Monel........	71	76	24	0	42
"	"	"	"	0.076	7
"	"	"	"	0.152	2

important in the case of lead, because arsenic-containing acid used in a plant might constitute some part of the feed to an acid reconcentrator. Experiments of short duration with chemical lead are summarized in Table II. It is seen that 0.1 percent As_2O_3 in the acid has no significant influence on corrosion even under conditions of acid strength and temperature that are highly corrosive to lead. Behavior of Admiralty brass appeared unaffected by addition of arsenic to 71 percent H_2SO_4 at 77° C.; the arsenic appears to have decreased the attack on Monel.

It might be thought that, because metallic arsenic plates out on steel as a hard resistant coating, protection for a considerable time might be gained by infrequent periodic treatment of the steel with arsenic-containing acid. Experiments along

these lines have shown that protection by this procedure is of only very short duration and that satisfactory results are obtained only when arsenic is present continuously in adequate concentration in the acid. It follows also that the initial dosage of arsenic must be quite high since a considerable portion of the arsenic first added will be removed from the acid by the steel equipment.

Conclusion

Trivalent arsenic compounds, such as arsenic trioxide or sodium meta-arsenite, behave as effective inhibitors of corrosion of carbon steel by hot, strong sulfuric acid under many conditions that may be employed in petroleum processes. Arsenic has been shown to be capable of substantially preventing corrosion of steel by acid concentrations in the range from 50 to 72 percent sulfuric acid at temperatures up to 85° C., even under high velocity flow conditions. It is less effective as an inhibitor in acid strengths around 88 percent sulfuric acid. The concentration of arsenic needed to suppress corrosion increases as the concentration of sulfuric acid is decreased, as temperature increases, and as trace contamination of the acid with copper increases. No evidence of pitting action was detected when general corrosion was completely suppressed.

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A Message from Your Officers

This Month's Contributor
F. L. LaQUE, Vice President NACE

IT IS INEVITABLE that those persons trying to promote the further growth of NACE will encounter questions as to the reality of the need for still another technical society.

Such questions are most likely to be raised by individuals who are particularly interested in some other organization and especially by those who fear that the NACE is encroaching on their territory or threatens to displace them from a particular field of activity.

Those of us active in the affairs of some of these other societies have had to examine these questions for our own peace of mind. Perhaps, therefore, some comments may be of help to other members of the NACE who may be called upon to discuss this subject in their efforts to secure additional active support for the NACE.

No one can seriously question the desirability of providing a means by which those engaged in the constant war against corrosion can exchange experiences from apparently unrelated fields but which, when brought together, may be found to be mutually significant and helpful. The means for such exchange can be provided most readily by an association concerned with corrosion wherever or however it may occur. Only an association of this character can assemble in its meetings the specialists in corrosion from several industries who otherwise might confine their public activity in the field to talking to each other without realizing that the solution to a similar difficulty being discussed by another group of specialists at another meeting could be applied effectively to their problem.

A natural corollary to this is that only an association concerned primarily with corrosion can devote the whole of its technical publications or journals to matters related to corrosion and, thereby, effect a concentration of information on the subject that is bound to be helpful to anyone seeking published information or references to it. The NACE journal, CORROSION, through its publication, not only of NACE contributions, but of important papers that appear elsewhere plus the most complete abstract coverage of the important corrosion literature would, of itself, be sufficient justification for the existence of the NACE.

It is true, that many other technical societies devote considerable attention to corrosion. But it is true also, that this attention tends to be spasmodic and the time allotted to corrosion at national meetings and the space provided in

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publications fall far short of serving the interests of those engineers primarily concerned with corrosion problems and of those executives who realize that attention to corrosion is currently one of the most effective means of securing relief from a drain on profits.

In line with their traditional activities and the nature of their members, there are two other technical societies that devote a considerable amount of attention to corrosion. These are "The American Society for Testing Materials" and "The Electrochemical Society."

ASTM is pre-eminent in the development of testing methods, and of specifications related to them. Committees of this society have also been active for many years in carrying out field tests of metals, alloys and protective coatings in localities representing a wide range of atmospheric conditions and to a lesser extent in such other natural environments as fresh and salt water. There is no need for the NACE to endeavor to parallel these activities of the ASTM. Instead, NACE can simply take advantage of this work by the ASTM by applying ASTM methods and data to the attack on those many other problems in corrosion that are outside the scope of the ASTM and which might not receive the benefit of organized attack if the NACE were not to sponsor it. This cooperation and avoidance of duplication of effort already is being assured by the number of people who have taken a prominent part in ASTM affairs and who are now equally active in the NACE.

The Corrosion Division of the Electrochemical Society is only a little older than the NACE. The character and interests of the members of this Division make it natural that this organization should concentrate its attention on the theory and fundamentals of corrosion and thus provide the Corrosion Engineers with the broad principles which will enable them to arrive more readily at sound solutions to the practical problems that will engage their attention. The supplementary nature of the two organizations is illustrated particularly well by their joint sponsorship of a symposium on cathodic protection, to be held in Pittsburgh later this year. The Electrochemical Society contributions will concentrate on basic principles while the NACE papers will feature their practical applications.

In addition to the national organizations concerned in some way with corrosion, groups of individuals have gotten together from time to time, in some cities, to hold technical meetings to discuss corrosion and what to do about it. The organization of these groups representing in their membership people who belong to one or more technical societies, is merely another reflection of the need being filled now by the NACE. With the formation of Local Sections of the NACE, the need for these informal and unattached groups disappears, since the NACE Local Sections will provide everything that is needed by way of organization and a continuing program tied in effectively with the activities of corrosion engineers on a national scale.

A canvass of the membership of the NACE will disclose that practically every member belongs also to one or more other technical organizations. Each of these, more than a thousand individuals, has discovered that the NACE provides something he needs that doesn't exist elsewhere. This combined testimony, impressive as it is, is merely another indication of the magnitude and importance of the universal problem which remains the basic justification for the existence and steady growth of a National Association of Corrosion Engineers.

F. L. LaQue

Vice President NACE

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NACE News

Report on Western Division Meeting

THIRTY-ONE members of the National Association of Corrosion Engineers and 29 guests attended the second annual regular meeting of the Western Regional Division of the Association, held June 4 at the Roger Young Auditorium, Los Angeles, Calif. Chairman Vance Jenkins presided. C. N. Gregory, Jr., Southern Counties Gas Company of California; J. T. Nicholson, District Engineer of National Aluminate Co., and R. W. Fouraker, Richfield Oil Corp., were guest speakers.

Mr. Gregory, whose paper was titled, "A Practical Application of Chemical Anodes as Part of A Cathodic Protection System," described a chemical anode assembly consisting essentially of a series of transite pipes installed vertically in the earth, filled with sodium hydroxide solution, inside of which (in a centralized position) were installed iron pipes, which pipes were connected to the output side of a rectifier. The advantages expected from such an assembly are (1) that it will be non-deteriorating, and (2) be of low resistance. One aspect that might be considered a disadvantage is that the sodium hydroxide solution must be periodically replenished. The installation is made in soil varying from 100 to 500 ohms cms, resistance, containing considerable moisture which is essentially sea water. Considerable discussion developed, and the interest of the audience was such that it was decided a subsequent report would be made after more operating data are obtained. Mr. Nicholson's paper, "Recent Developments in the Use of Corrosion Inhibitors," included points on corrosion testing apparatus, methods of evaluating corrosion, and mitigation measures; besides various expedients for corrosion prevention, including selection of metals, treatment of water, cathodic protection, protective paints and use of film-forming materials.

Mr. Fouraker gave a brief discussion on "Evaluation of Corrosion Inhibitors." He brought out the point that tests should be run before as well as during the use of inhibitors, and that corrosion nipples (to evaluate effectiveness of mitigative measures) should be of the same material as the system itself.

The next meeting of the Western Division has been tentatively scheduled for the latter part of September, at which time consideration of officers for 1947-48 will be among the business points taken up.

TWO NEW SYMPOSIA ADDED TO TECHNICAL PROGRAM
FOR 1948 NACE ALL-CORROSION CONVENTION

EVER expanding the scope of the Association, and creating a greater medium for the exchange of information on the subject of corrosion as affects all industry, officers of the National Association of Corrosion Engineers accepted the suggestion of M. G. Fontana, Chairman of the Technical Program Committee, to add two new symposia to the list of technical subjects which will be presented during the 1948 Convention and Exhibition, to be held at the Hotel Jefferson, St. Louis, Mo., April 5, 6, 7 and 8.

These new symposia, Protective Coatings for Metals, and Salt Water Corrosion, increase to ten the number of subjects on which technical papers will be presented. The other eight sessions will be on Cathodic Protection, Chemical, Communications, Electrical, Gas, Oil, Water and General industry.

An outstanding program is being arranged for the April 5 to 8 meeting, and papers will be both research and practical in nature.

It is planned that four papers of 30-minutes length each will be presented during each session, with 15 minutes allowed for discussion on all papers. Invitations already have been forwarded by session chairmen, as the deadline for manuscripts has been tentatively set for January 1, 1948. This date has been set because the Publication Committee of

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Regional Organization Completed

THE FIFTH and last Regional Division of the National Association of Corrosion Engineers came officially into existance June 30 when, at a meeting held in Atlanta, Georgia, and presided over by Tom L. Holcombe, Chairman of the Membership Control Committee of NACE, members who reside in the South East Division area, comprising the States of Alabama, Georgia, Mississippi, South Carolina, Tennessee, Florida, Kentucky, North Carolina and Virginia, nominated and elected officers and drew up By-Laws for the Region in accordance with the Articles of Organization and By-Laws of NACE.

Officers elected were: E. B. Ayers, Atlanta, Chairman; James T. MacKenzie, Birmingham, Vice Chairman; Alan C. Nelson, Atlanta, Secretary-Treasurer. H. C. Van Nouhuys, Atlanta, was named Chairman of the Membership Committee, and Ivy M. Parker, Bremen, Ga., was appointed Chairman of the Program Committee.

The next meeting of the South East Region is tentatively scheduled for October of this year, at which time provisions will be made for nomination and election of officers who will take up duties January 1, 1948. Provisions will be made for those members unable to attend the meeting to make nominations and vote by mail.

The June 30 meeting was attended by various officers of the parent Association, including President G. R. Olson, Vice President F. L. LaQue, Treasurer O. C. Mudd, Executive Secretary A. B. Campbell and Directors L. A. Baldwin and Mr. Holcombe.

NACE plans to have abstracts of all papers available in advance of the St. Louis meeting.

Members of all committees participating in arrangement of the technical program have been announced by Mr. Fontana as follows:

Technical Program Committee

>M. G. Fontana, Chairman, The Ohio State University, Columbus, Ohio.

>A. Wachter, Co-Chairman, Shell Development Co., Emeryville, Calif.

>F. A. Rohrman, Co-Chairman, University of Colorado, Boulder, Colo.

>F. L. LaQue, International Nickel Co., New York City, N. Y.

>R. B. Mears, Co-Chairman, Carnegie-Illinois Steel Corp., Pittsburgh, Pa.

Cathodic Protection Symposium

>R. A. Brannon, Chairman, Humble Pipe Line Co., Houston, Texas.

>R. J. Kuhn, Co-Chairman, Consulting Engineer, New Orleans, La.

>H. A. Robinson, Co-Chairman, Dow Chemical Co., Midland, Mich.

>I. C. Dietze, Co-Chairman, Dept. of Water & Power, Los Angeles, Calif.

Chemical Industry Symposium

>W. C. Fernelius, Chairman, Purdue University, Lafayette, Ind.
>N. E. Berry, Co-Chairman, Servel, Inc., Evansville, Ind.

Cleveland Section Formed

● **L. F. Greve, Chairman of the North Central Regional Division of the National Association of Corrosion Engineers, advised that members of the Association who reside in Cleveland, Ohio, convened as a Local Section to elect officers as follows: Everett C. Gosnell, Section Chairman; Donald A. Scanlon, Section Vice Chairman; and C. E. Heil, Section Secretary-Treasurer. H. H. Febrey was named Chairman of the Cleveland Section's Program Committe, D. J. Connelly was appointed Chairman of the Membership Committee, and C. J. Warner heads the Entertainment Committee. The Secretary of the new Section can be addressed care of Heil Process Equipment Corporation, 12901 Elmwood Avenue, Cleveland 11, Ohio.**

Communications Symposium

>L. B. Routson, Chairman, Western Union Telegraph Co., Chicago, Ill.

>W. C. Honecker, Co-Chairman, Indiana Bell Telephone Co., Indianapolis, Ind.

>W. F. Bonner, Co-Chairman, Federal Telephone & Radio Corp., Newark, N. J.

>D. T. Jones, Co-Chairman, Southern California Telephone Co., Los Angeles, Calif.

Electrical Industry Symposium

>L. J. Gorman, Chairman, Consolidated Edison Co., New York, N. Y.

>G. A. Mills, Co-Chairman, Central Power & Light Co., Corpus Christi, Texas.

>G. P. Gamble, Co-Chairman, Union Electric Co., St. Louis, Mo.

>E. V. Sayles, Co-Chairman, Consumers Power Co., Jackson, Mich.

Gas Industry Symposium

F. J. McElhatton, Chairman, Panhandle-Eastern Pipe Line Co., Kansas City, Mo.

F. A. Rohrman, Co-Chairman, University of Colorado, Boulder, Colo.

C. A. Goldkamp, Co-Chairman, San Diego Gas & Electric Co., San Diego, Calif.

General Industry Symposium

R. M. Hunter, Chairman, Dow Chemical Co., Midland, Mich.

C. B. Smith, Co-Chairman, Dearborn Chemical Co., Chicago, Ill.

F. L. LaQue, Co-Chairman, International Nickel Co., New York City, N. Y.

Oil Industry Symposium

A. Wachter, Chairman, Shell Development Co., Emeryville, Calif.

Corrosion Congress Contribution

● To further formalize the direct cooperation between the National Association of Corrosion Engineers and Commission Technique des Etats et Proprietes de Surface des Metaux, Paris, France, a letter has been forwarded to M. Perreau, Secretary of the French Association, by NACE President, G. R. Olson, indicating that papers prepared by several members of NACE would be presented at the International Corrosion Congress, to be held in Paris in October this year. Among those persons who will prepare papers are F. L. LaQue, R. B. Mears, M. G. Fontana, G. H. Young, and F. N. Speller. Mr. Speller has consented to have his paper presented as a direct contribution from NACE to the French Society.

J. C. Stirling, Co-Chairman, Stanolind Pipe Line Co., Tulsa, Oklahoma.

M. S. Northup, Co-Chairman, Standard Oil Co., Elizabeth, N. J.

J. M. Pearson, Co-Chairman, Sun Oil Company, Chester, Pa.

Protective Coatings for Metals Symposium

G. W. Seagren, Chairman, Mellon Institute, Pittsburgh, Pa.

G. Diehlman, Co-Chairman, National Lead Co., Research Labs., Brooklyn, N. Y.

A. H. Thomas, Co-Chairman, American Rolling Mill Co., Research Labs., Middletown, Ohio.

Salt Water Corrosion Symposium

C. P. Larrabee, Chairman, Research Lab., Carnegie-Illinois Steel Corp., Vandergrift, Pa.

M. Mosher, Co-Chairman, Bethlehem Shipbuilding Co., Quincy, Mass.

E. S. Dixon, Co-Chairman, Texas Company, Port Arthur, Texas.

Water Industry Symposium

A. H. Ullrich, Chairman, Water Dept., City of Fort Smith, Fort Smith, Ark.

F. E. Dolson, Co-Chairman, St. Louis County Water Co., St. Louis, Mo.

V. V. Kendall, Co-Chairman, National Tube Co., Pittsburgh, Pa.

R. M. Ashline, Co-Chairman, Dept. of Water & Power, Los Angeles, Calif.

TENTATIVE CATHODIC PROTECTION SYMPOSIUM PROGRAM SPONSORED JOINTLY BY NACE AND ECS ANNOUNCED

The tentative program for the Cathodic Protection Symposium, sponsored jointly by the National Association of Corrosion Engineers and the Corrosion Division of the Electrochemical Society, has been announced. As of July 1, there had been 22 definite acceptances of papers to be presented during the meeting, which will be held December 8, 9, and 10, 1947, at the William Penn Hotel, Pittsburgh, Pa. Twelve of the definite acceptances thus far received are from members of NACE, while the other ten are from ECS members. Three NACE papers are awaiting acceptance, while one NACE paper and two ECS papers are unassigned. The tentative program follows:

1. Electrochemical Principles of Cathodic Protection*
   R. H. Brown, Aluminum Co. of America, New Kensington, Pa.
2. Characteristics and Field Use of Electrical Instruments†
   M. C. Miller, Ebasco Services, Inc., New York, N. Y.
3. Characteristics of Half Cells Used as Reference Electrodes*
   P. Fugassi, Carnegie Institute of Technology, Pittsburgh, Pa.
4. Laboratory Methods for Determining Current Density Required for Cathodic Protection*
   R. B. Mears, Carnegie-Illinois Steel Corp., Pittsburgh, Pa.
5. Null Method of Determining Current Density Required for Cathodic Protection†
   R. F. Hadley, Susquehanna Pipe Line Co., Philadelphia, Pa.
6. Detection, Measurement and Mitigation of Stray Currents*
   F. B. Fry, Public Service Co. of Colorado, Denver, Colo.
7. Detection and Measurement of Currents Other than Stray Currents, Including Magnetic Earth Currents†
   Lyle Sheppard, Shell Pipe Line Corp., Ferriday, La.
8. Advantages and Disadvantages of Various Current Sources†

   G. R. Olson, United Gas Pipe Line Co., Shreveport, La.
9. Choice and Installation of Anodes†
   Derk Holsteyn, Shell Oil Co., Deer Park, Texas.
10. Fundamental Characteristics of Zinc Galvanic Anodes*
   E. A. Anderson, New Jersey Zinc Co., Palmerton, Pa.
11. Characteristics of Zinc and Aluminum Galvanic Anodes in Sea Water*
   T. P. May, U. S. Naval Research Laboratories, Washington, D. C.
12. Fundamental Characteristics of Aluminum Galvanic Anodes*
   E. D. Verink and R. B. Hoxeng, Aluminum Co. of America, New Kensington, Pa.
13. Fundamental Characteristics of Magnesium Galvanic Anodes*
   A. Smith, The Dow Chemical Co., Midland, Mich.
14. Behavior of Experimental Zinc-Iron Couples Under Ground*
   I. A. Denison, National Bureau of Standards, Washington, D. C.
15. Practical Use of Galvanic Anodes†
   H. Walquist, Ebasco Services, Inc., New York, N. Y.
16. Application of Cathodic Protection to Water Tanks, Process

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Tear Out Form

R. B. MEARS, Manager,

Research Laboratory,
Carnegie-Illinois Steel Corp.,
210 Semple Street,
Pittsburgh 13, Pa.

Vessels and Miscellaneous Equipment†
Electro Rust-Proofing Corp., Belleville, N. J.

17. Relations Between Protective Coatings and Cathodic Protection†
Guy Corfield, Southern California Gas Co., Los Angeles, Calif.

18. Coordination of Cathodic Protection Installations to Avoid Interference with Adjacent Structures†
L. B. Nelson, Shell Pipe Line Corp., Cushing, Okla.

19. Cathodic Protection in Control of Stress-Corrosion Cracking*
H. J. McDonald and R. D. Misch, Illinois Institute of Technology, Chicago, Ill.

20. The Use of Rectifiers as an External Source of Protective Currents†
F. A. Waelterman, Benwood-Linze Co., St. Louis, Mo.

21. The Mitigation of Corrosion on Underground Cable Systems†
L. J. Gorman, Consolidated Edison Co., New York, N. Y.

22. Potential Distribution in Cathodic Protection Systems*
Gordon N. Scott, Consulting Engineer, Los Angeles, Calif.

23. The Use of Wind Driven Generators as an External Source of Protective Currents†
M. L. Jacobs, Jacobs Wind Electric Co., Minneapolis, Minn.

24. The Use of Engine Driven Generators as an External Source of Protective Currents†
Lon Wainman, El Paso Natural Gas Co., El Paso, Texas.

25. Economic Factors Bearing on Application of Cathodic Protection†
A. N. Horne, Texas Empire Pipe Line Co., Tulsa, Okla.

26. Structure-to-Soil Potentials as a Method of Determining Current Density Required for Cathodic Protection†
Scott P. Ewing, Carter Oil Co., Tulsa, Okla.

27. Theoretical Aspects of Current Distribution in Cathodic Protection*
J. M. Pearson, Sun Oil Company, Chester, Pa.

28. Biochemical Corrosion as Related to Cathodic Protection*
(Subject unassigned at time of this report.)

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* ECS acceptance.   † NACE acceptance.

Excepting items 23, 24 and 25 above, which are awaiting acceptance, and items 26, 27, and 28, which are unassigned (it is believed the persons listed will accept items 26 and 27) all other papers have been definitely accepted.

It is predicted by the most conservative that this three-day Cathodic Protection Symposium will draw a record crowd.

In order that more definite arrangements can be made with the hotel regarding the number of rooms which should be reserved for this meeting, it is desirable to obtain a preliminary *estimate* of the number of people who plan to attend the meeting and who will require rooms.

If you believe you *may* attend this symposium, please tear off the form below, fill it out and mail it *today* to R. B. Mears, whose address is printed on the reverse side of the form.

Tear Out Form

Gentlemen:

I am planning to attend the Cathodic Protection Symposium at the William Penn Hotel in Pittsburgh, Pa., December 8, 9 and 10, 1947.

*Signed*_____

General Interest

R. W. C. Whalley, corrosion engineer associated with the Iraq Petroleum Company, Haifa, Palestine, and a member of NACE, is on an extended visit to the United States for purpose of studying corrosion control methods used in this country for possible application to his company's oil transportation pipelines. Mr. Whalley, on a visit to the Houston headquarters of NACE, stated that corrosion has developed into a serious problem on the Iraq lines, and his company is expending large sums of money to put down the toll and maintain lines in operating condition. Iraq Petroleum operates 1200 miles of pipelines, comprising 12-inch lines from Kirkuk, Iraq to Haifa, Palestine, and Tripoli, Lebanon, above Haifa on the Mediterranean coast. The lines traverse various types of terrain and pass through a wide range of soil conditions. Shallow salt deposits have created a serious problem on all lines. The present 12-inch carriers will be augmented by the addition of parallel 16-inch lines, and it is the company's intention to employ the latest corrosion prevention methods on these new lines, to prevent as much as possible the losses incurred on present lines. He plans to visit a majority of the oil corrosion laboratories in this country before going to London, England, location of his company office, then returning to Haifa.

The annual Symposium on Corrosion and Metal Protection will be held at Hotel Carter, Cleveland, Ohio, Saturday, September 27, 1947. The meeting is open to all interested persons, and a record-breaking attendance is expected, according to E. C. Gosnell, chairman of the recently established Cleveland Section of the National Association of Corrosion Engineers and Program Chairman for the Cleveland technical meeting. He also reports that an interesting group of papers pertaining to corrosion and protective coatings will be presented by nationally known authorities in their fields. The tentative program will appear in the September edition of CORROSION.

The Tapecoat Company, Evanston, Ill., has appointed James E. Mavor, Houston, Texas, and Gene McIntyre, Los Angeles, Calif., to represent Tapecoat pipe joint protection material. Mr. Mavor will handle distribution of Tapecoat in the mid-continent field through his own representatives; F. P. Kelly, covering Louisiana and East Texas, and Robert Lingle, Corpus Christi. Mr. McIntyre will represent the company in California, Washington, Oregon, Nevada and Arizona.

New Technical Committees

● At a meeting of the Technical Practices Committee, held July 12, 1947, in Pittsburgh, Pa., six new technical committees were activated to study various industrial corrosion problems, according to a report made by Committee Chairman R. B. Mears, of the Carnegie-Illinois Steel Corp. The new committees are as follows: Minimum Current Requirements for Cathodic Protection; Corrosion Problems Involved in Processing and Handling Chemicals; Protective Coatings; Corrosion Problems Involved in Inland Waters; Prevention of Corrosion by Means of Inhibitors, and Materials for Use at High Temperatures.

On the Other Side of the Fence*

By Tom L. Holcombe*

IT WOULD be a gross distortion of the truth, if I should say as is customary on these occasions, that it is a pleasure to address you. The words, pleasure, privilege, honor or any other descriptive noun which I might select would be totally inadequate. To have the master minds of the corrosion world silenced before you, even for just a few minutes, while you tell them something, any salesman would gladly sacrifice all his heavenly hopes. I realize, of course, that that silence is only temporary. But nothing shall cause me to decline this opportunity. Not even the presence of my Boss.

I want to talk about NACE, and I want each of you to think about NACE. I want to bring to you, in a general way, the status of our present position and what you, as a Member, may do to improve and expand our activities and our growth.

As all of you undoubtedly know, we were organized in 1943 by a group of men associated with problems of corrosion control. These men, who were then associated with other organizations, recognized the need for an association of a wider scope, devoted exclusively to the

rapidly developing branch of engineering dealing directly with corrosion in its various phases; recommend accepted practices, formulate policies and exchange information for the mutual solution of corrosion problems.

From this plan of simple reasoning and sound doctrines, articles of organization and by-laws were established. We are a voluntary, non-profit organization, but representing industries which must have profits, even during periods of unstable economy, and despite many forms of regulation that have been thrust upon them.

Since 1943, we have come a long way. Under the guidance of the pioneer group, the membership has surpassed 1000 competent engineers. Millions, even billions of dollars, so the experts tell us, are lost annually because of uncontrolled corrosion. Certainly, our organization is well justified, and it is little wonder our membership is growing phenomenally.

Now, with all our growth, we are suffering from growing pains and our financial condition is not entirely satisfactory. Many of us have not told or sold our respective companies on the real value of an associate or corporate membership. The present ratio of our active memberships to associate and corporate memberships is about 10:1. It is our opinion

that for each total of four active memberships there should be one associate or corporate membership.

I know many of your members of management have asked you, why should we spend $100 per year when you can get the benefits of the Association for $7.50 per year. From an economic standpoint that sort of reasoning may make sense—temporarily. In the long run, however, the real benefits of the Association will cease and none of us will have accomplished very much. Somehow or in some way our managers must be made to realize that a wee bit of gambling is necessary. In short they must place on us a $100 bet each year and trust our ability to come through.

Additional Revenue Needed

Permit me to tell in a general way, but briefly, some of our needs for the NACE, and why we are asking for additional revenue.

The Executive Secretary, A. B. Campbell, is endeavoring to administer the central office as economically as possible. But he needs help. By that I mean sufficient help to permit his leaving the office occasionally to visit your region, to know you better and determine to some extent your needs from the home office. He needs to solicit and cultivate new memberships and more advertising, but these things cannot be done until more money is available.

Our magazine CORROSION is not self-supporting. The present advertising sales do not furnish more than 50% of the revenue required to cover the cost of our publication. The result is, membership dues must be used to subsidize the cost of the magazine publication. This sort of condition is anything but healthy. We must have added advertising sales and we must maintain the required volume of such sales until a much larger membership is acquired. Meanwhile, we should not be ashamed to offer for sale advertising space in our magazine. Every reader is either a customer or a very live prospect, which constitutes the type of readers the manufacturers want to reach. Then too, the advertising will keep you abreast of new and improved products as they are developed.

I am sure each of you read the abstracts which are published in the magazine each month. These abstracts are taken from worthwhile articles dealing with corrosion control and compiled by Dr. Ivy Parker. This compilation is very time consuming. It is imperative that the Association provide funds to insure the continuation of this valuable project.

How to Facilitate Work of Committees

Some time ago technical committees were appointed and assigned to the various problems of corrosion control deemed to require immediate attention. The men on these committees are working, but their progress is abnormally slow because they need help to calculate the details that necessarily enter into projects of this type. To expedite this work and show tangible signs of progress we need to have on the Association's payroll one or perhaps two competent engineers to work with the technical committees, to assist in ferreting out the details. Here too,

added expense will necessarily be incurred and extra revenue will have to be raised.

The work of the technical committees and their expected accomplishments is the one MUST of our Association. Out of their experiments and calculations it is hoped to effect some standardization in corrosion control. Such an accomplishment would be a great step forward for our Association; and to be sure, it will justify the $100 per year to be paid by various firms for corporate or associate membership.

On Standardization

By calculations, the engineer will sooner or later, adopt some form of standardization. Only, however, if he is fortunate enough to avoid theoretical blunders which prove that the feat can be accomplished in a manner already adopted by his companion—the practical operator.

Actually, this plan of standardization should include all the essentials. We know that. But for the sake of progress, let us begin to think about trying something immediately and lay aside the law of probabilities. Somehow, we can make provisions for the eventualities if and when they occur.

Many Jobs Yet to Be Done

Frankly speaking, there are many jobs yet to be done. We need a minimum of 150 new associate and corporate memberships; and we need to double the present advertising sales in our magazine. So the big question is, on whom may we depend to assist us in these undertakings? Our only answer is, to look to the NACE membership from whence must come our help.

It is not my intention to get personal, but—what are you doing to aid in the functions of NACE? Perhaps I am not fully justified in asking this question, but let me say this to you. You know without again being informed, I was appointed General Chairman of this conference along with Committee Chairmen, Co-Chairmen and Workers. All those who accepted assignments to work with our Annual Conference have done an excellent job, as exemplified in the Technical Program and Exhibition. Our Annual Conference, however, constitutes only a small portion of the work which must be carried on daily if our plans are to be perfected and our ultimate goal is attained. Within the operations of this organization there are many jobs besides the Annual Conference. And I am frank to tell you, to date, we are working with only a skeleton crew.

Let "George" Do It

It has been and still is pretty much of a makeshift proposition. In practically every instance when we asked someone to accept an assignment or perform a job, there comes the old cry, "too much to do," "absolutely no time" and "entirely too busy."

In Roark Bradford's book "Ole Man Adam and His Chillun," from which the play "Green Pastures" was taken, the old negro preacher tells you that the Lord created the heavens and the earth in seven days. He then looked upon his work and called it good, all because even the Lord realized that he had completed a pretty sizeable job. Realizing this fact, he turned to some of his people

and said, "There is a heap of fine land around here and somebody's got to work this land." The old preacher further tells you that Gabriel was the type who dodged responsibility and therefore anticipated the Lord's request by saying, "Lord, I would ask for the job, but I has to practice on my horn all the time."

I like to tell that story. Therein lies 20th century evil—Alibi! Most of us will admit that our present system is to let "George" do it. Why? Could it be that such an attitude is an intrinsic characteristic? More than likely many are modest and hesitant about doing something which we should really 'ke to do. Only you have the answer; and I think the moment apropos for considering and analyzing what we have to offer and work with in this Association.

A Salesman Can't Let "George" Do It

If you encounter difficulty in your self-analysis on ways and means to make use of your talents, permit me to offer this suggestion. Go to your management and request that they make arrangements to have you transferred from your engineering operations to the sales department. After you have become a member of the sales force have the sales manager start you selling and be sure he sends you on the road. You will receive a most liberal education. You will learn that if you let "George" do the little extras, your competitor will get the business.

For almost twenty years I was on the other side of the fence, helping to build pipelines, drill oil and gas wells and finally preparing budgets. Learning as much as I did from budget procedure and the handling of finance, I never fully realized until the past few years that somebody has to sell the company's products and collect the money before any of us can be paid. This sales work must go on in every shop, in every store and in every organization if prosperity and profits are to be attained. Every salesman and every member of management will agree. The whole world, whether you recognize it or not, is dependent on selling.

The Fit Survive

When you have learned to sell with simple dignity and just average intelligence your analysis is very nearly completed and your problem pretty well mastered, all because as you would find, you must produce or starve.

With all I have said and the unfavorable impressions I may have imprinted in your minds, do not misunderstand me. The progress to date has been good. However, let us all remember and bear in mind, nothing stays good unless we use every effort to make it better. We want to become more than just another association. We want to keep the Association on a high level, and conduct its affairs in a manner commensurate with the best engineering practice.

Work and Grow

The whole group of us must shoulder and assume the responsibility of our prorata share. We simply cannot stop where we are and hope that George will carry on. Ours is a young organization. We are not infallible and none of us is immune

to mistakes. Actually the crying need is for more fight, more workers, greater results and just the opportunity to correct a few mistakes.

Naturally, I know many of you do not like the word salesmanship. Because of personal circumstances, I dislike to mention it, yet the goods of NACE must be sold to more people and particularly those who can pay $100 per year, if we expect to be shoved off center without further delay. The proper volume increase could create a substantial reduction in unit cost. It will enable us to enlarge our office force, to place the magazine on a self-sustaining basis, and make greater progress in the field of research.

Field Is Wide Open

What we have built thus far is needed and our field of opportunity is wide open. There are some who may say we already have too many organizations; that the work we are doing is a repetition of that done by other associations much older than ours. The only thing I have to say about such an argument is that we definitely need an association devoted exclusively to corrosion control. Already we have as members the cream of the engineering talent within the varied industries; and a firm foundation has been laid. The extra workers and extra revenue we now need

is our only besetting sin, at least currently.

Looking down the road, I see this sign. Barring another war within the next few years, the experts tell us, many new metallic structures will be built; and business will be good. Through and from the knowledge gained in our Association work, these structures may well be given proper protection. In the years to follow the huge construction program, the experts tell us again, that business will not be so good, that earnings will show a decided decline. It is then, as in 1932 and '33, management and operators will become keenly conscious of each expenditure and employ all their ingenuity to lower the cost of operations and maintenance. With this outlook, where could we better fit into the picture. What could be more appreciated by our management than the lowest possible maintenance cost when the going is tough and every savings is an asset.

Final Question

You have heard the questions, you have been made aware of our needs, you have been told of our opportunities and what your personal efforts can mean in making our Association a real leader in industry and conserving our natural resources. One final question, Gentlemen of NACE—What are you going to do about it?
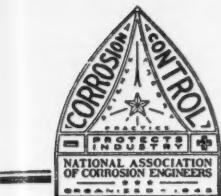
ATMOSPHERIC CORROSION

Corrosion and Protection of Iron and Steel. G. TOLLEY, J. Birmingham Met. Soc., **25,** 81-114 (1945) ; Brit. Abs., **BI,** 245 (1946) July.

A general survey of the atmospheric corrosion of iron and steel and the use of paints and metallic coatings for protection.—INCO.

Symposium on Atmospheric Exposure Tests on Non-Ferrous Metals. 145 pages. 1946. American Society for Testing Materials, Philadelphia, Pa.

Six papers and their discussions present data resulting from tests carried on over a ten-year period. The resistance of rolled zinc, nickel and Monel, copper, lead and tin, and aluminum-base alloys to atmospheric corrosion covered in the first five papers. The last paper describes the use of statistical methods in evaluation of corrosion test data, and the discovery of reasons for erratic variations in the data. Appendices contain pertinent excerpts from previous reports.—BLR.

CHEMICAL CORROSION

The Relationship Between Welding and the Corrosion of Stainless Steels. A. DESY, Rev. Soudure, **I,** 2, 3-26 (1945).

The tests described demonstrate the possibility of reduction of corrosion-resistance by incorrect welding conditions.—INCO.

Significance and Evaluation of Atmospheric Corrosion Tests on

Carbon and Low-Alloy Steels. K. F. DAEVES, K. F. MEWER AND E. H. SCHULZ, Korros. u. Metallschutz, **19,** 233-257 (1943) ; Brit. Abs., **B-1,** 423 (1946) Dec.

Results of outdoor corrosion tests in Germany, Britain, and U.S.A. tabulated and compared. Results include tests on ingot irons, carbon steels and steels containing small additions of copper, chromium, molybdenum, silicon, and nickel, in various atmospheres using sheet and wire specimens. To assist in the correlation of future tests, it is suggested that a standard for comparison, such as ingot iron, should be selected, and that all the test conditions should be specified. Conclusions are given.—INCO.

Kraft Mill Maintenance. W. McINTOSH, JR., Paper before Tech. Assoc., Pulp & Paper Inds., meeting, Milwaukee, Wis., Oct. 2-4, 1946. Paper Trade J., **123,** 15, 180-182 (1946) Oct. 10.

Corrosion problems are described and choice of materials discussed. Among materials used for liquor piping are stainless steel, Monel, cement-lined steel pipe, cast iron with low nickel content and Ni-resist. Mention of service life made.—INCO.

Nickel, Nickel Alloys (in Acetic Acid). W. Z. FRIEND. Corrosion Forum Symp. "Acetic Acid vs. Materials of Chemical Plant Construction-II," Chem. Eng., **53,** 12, 218 + (1946) Dec.

Results of laboratory tests of Monel,

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nickel, Ni-resist and Inconel in aerated, unaerated acetic acid at varying temperatures and concentrations, as well as plant tests in various reactions involving acetic acid are discussed. Monel has good resistance to all concentrations of unaerated acid at room temperature. Corrosion rate rises with aeration and is most active with concentrations of 50% acid. Nickel is resistant to unaerated acid of all concentrations at room temperature but increased temperature raises its corrosion rate more than Monel, and aeration is detrimental also. Inconel is useful with dilute solutions, but not with hot, strong solutions. Ni-resist is suitable for unaerated solutions at room temperature and in dilute solutions at high temperatures. Parts for each metal are mentioned.—INCO.

Electrolytic Fluorine Production in Germany. H. R. NEUMARK, Paper before Electrochem. Soc. 90th Gen. Mtg., Oct. 16-19, 1946, Toronto, Canada; Electrochem. Soc. Preprint **91-3**, 37-54 (1946).

A summary of the development of the elemental fluorine process in Germany during war is presented. The suitability of the various metals as anode materials including copper, iron, silver, nickel, magnesium and Monel is discussed and it is concluded that nickel is the most satisfactory metal up to 100° C. The factors affecting the operation and the life of different types of graphite anodes and studies on the characteristics of various electrolytes are discussed. Graphite is a suitable anode material at temperatures around 250° C. and specially prepared carbon anodes are used between 65 and 90° C. Operating details are given for two German cells. Metals investi-

gated for their use as cathodes in KF.HF electrolytes at 250° C. are silver, lead, copper, iron, nickel, brass and magnesium. Nickel shows considerable corrosion without current flow and the formation of nickel fluoride, which is soluble in water. The corrosion deposit has tendencies to blister. Under current flow at a current density of 45 amp./sq. ft., nickel shows only slight corrosion. Silver is the most satisfactory cathode material, and magnesium or elektron is the most suitable metal to be used for the construction of the electrolytic cell.

—INCO.

Manufacture of DDT—First Made in Ton Lots at the Chemical Warfare Laboratories in Ottawa. J. NEIL, A. K. AMES, AND A. E. MCILHINNEY, Chemical Warfare Labs. Confidential Report, June, 1945, released. Canadian Chem. Proc. Ind., **30**, 8, 77-80 (1946) Aug.

Preparation of DDT including: reagent specifications, plant procedure, control analysis and corrosion effects. At intervals during the production, all equipment was carefully examined to determine the extent of corrosion. No damage was visible in either the glass-lined or earthenware equipment. The cast-iron cock at the bottom of the Pfaudler kettle was serviceable after six months if the sulfuric acid had a minimum strength of 98.5% or lasted less than two weeks if used with weak acid. The ventilator hood and stainless steel shafts and propellers used for agitation, had to be replaced after six months. Stainless steel 24 mesh wire screen was found to be most resistant to attacks of strong acid and, therefore, was used for filtering.

—INCO.

Mechanical & Metallurgical Control of Sulfuric Acid Corrosion in Petroleum Processes. E. R. WILKINSON. Paper before ASME, Tulsa, Oct. 7-9, 1946, Petro. Processing, **1**, 3, 174 + (1946) Nov.; Oil & Gas J., **23**, 96 + (1946) Oct. 12; Corrosion **3**, 5, 252 + (1947) May.

The five basic factors which influence sulfuric acid corrosion are reviewed; acid concentration, acid temperature, oxygen content of fluid, velocities and turbulence of fluid and electrolytic action. Corrosion in acid treating and alkylation plants is greatest in the equipment for reclaiming, separating and concentrating. Muntz metal, everdur and Monel give good service. 18-8 chrome-nickel stainless, containing copper, molybdenum, or silicon or combinations thereof is also used. In sulfuric acid alkylation, corrosion occurs at points of abrupt changes of direction. The best solution is 18-8 chrome-nickel stainless steel, with steels containing molybdenum of superior value. In separators, Hastelloy D valves, while corrosion resistant, are poor from an operational standpoint because of their design. They are unsatisfactory where coke is encountered. The copper-bearing alloys, such as Monel, are poor in 60% acid at 275° F. Hastelloy D, corrosion, duriron, lead, acid brick and carbon have employed in the concentrators, depending on the exact conditions at various points. Summary of material suitability for specific applications in sulfuric acid service, from operating experience data is tabulated.—INCO.

Chemical and Heat Resistance of Gasket Materials. H. H. DUNKLE AND E. C. FETTER, Chem. Eng., **53**, 11, 102-109 (1946) Nov.

Service and other factors affecting gasket selection, gasket construction and materials are considered. Reaction of the following metals to heat and corrosion in gaskets is briefly described: Monel, nickel, platinum, lead, tin, aluminum, copper, brass, silver, ingot iron and low-carbon steel, stainless types 502, 410, 304, 347, 316. Non-metallic materials are also covered. A table lists chemical resistance of these materials to specific chemical reagents.—INCO.

Corrosion in Briner Economizers. J. T. MacDonald. Pulp & Paper Mag. Canad. **47**, 4, 60-61 (1946) ; Brit. Abs., **BI**, 214 (1946) July.

A summary of replies to a questionnaire from 27 mills (48 installations). Only 4 mills (10 installations) reported no noticeable corrosion. On an average, the life of the copper units is 3 times that of the Armco galvanized-iron units. Water sprays greatly improve efficiency of operation and reduction of fire hazard. Corrosion first appears as pinholes at the top and bottom joints and bottom outer casting.—INCO.

Corrosion of Copper Evaporator Tubes. J. Soc. Chem. Ind. **64**, 8 233-56 (1946) Aug.

The effect of the conditions on the steam and liquor sides have been investigated in detail in the case of iron and brass tubes. In brass tubes, local cells generally lead to dezincification and intercrystalline attack. The rate of attack can be related to such factors as internal strain in the material, the zinc content of the brass and variations in composition along the tube length. Attack on the liquor side is affected by the concentration of am-

monia, carbonates, chlorides and ni-
trates. On the steam side, ammonia
and carbon dioxide are the chief
agents in the corrosion. The rate of
attack in large plants depends on many
operating factors, but it seems prob-
able that the cause of the graded cor-
rosion along the heating tube is the
variation in liquor velocity along its
length.—CEC.

**Corrosion Limits Metals That Can
Be Used for Construction of Hy-
drofluoric Alkylation Units.** Phillips
Petrol. Co. "Hydrofluoric Acid Al-
kylation" (Bk.) Chapter 10; Nat.
Petrol. News, **38**, 32, Section 2, R-
618 + (1946) Aug. 7.

Summary of tests to show corrosive
effects of anhydrous and aqueous hy-
drofluoric acid. Effects of oxygen,
time, temperature, velocity of hydro-
fluoric streams are also discussed. Cor-
rosion rates in anhydrous hydrofluoric
acid are listed for Monel and "K"
Monel, nickel and Z-nickel, 30 and
20% copper-nickel, Inconel, AISI
types 302 and 317, cast 25-12 stainless
steel and others. Test data of Monel,
magnesium and silver in aqueous hy-
drofluoric acid are also tabulated. The
excellent service of Monel is stressed
and discussed in detail. However, both
Monel and copper-nickel corrode in
aqueous hydrofluoric acid. Hastelloy
A and B show intergranular corrosion,
and Ni-resist graphitization. Two un-
solved problems are blistering of steel,
presumably by hydrogen, and break-
age of bolts, studs, etc. Service tests
belied laboratory indications that 18-8
would stand up as thermowells at 300°
F. Corroding agent may be fluosilicic
acid or aqueous hydrofluoric acid. "K"
Monel studs, heat-treated, or Stellite-
coated plugs are recommended. Man-

ning, Maxwell and Moore Alloy No.
7 (40% nickel—44.6% copper—10.0%
tin—0.10% silicon—.03% phospho-
rus) is mentioned. Its corrosion re-
sistance was adequate in relief valves,
but insufficient in ring-joint connec-
tions. Stress corrosion of 18-8 oc-
curred only in aqueous hydrofluoric
acid.—INCO.

COATINGS

**Chromates in Metal Protective
Paints.** HANS WAGNER, Farben Ztg.,
47, 177 + (1942); Paint, Oil &
Chem. Rev., **109**, 49-50 (1946) Dec.
12.

The improvement of priming paints
by use of small percentages of chro-
mates was the subject of extensive
German research. Numerous steel pan-
els were painted, using various paint
formulations and given outdoor ex-
posure tests. Results are outlined.—
BLR.

**Urea-Formaldehyde Coating Res-
ins and Products with Which They
Are Used.** O. P. CLIPPER, Paint &
Varnish Prod. Manager, **26**, 310-311
(1946) Dec. A review.—BLR.

Tinning Cast Iron. Iron Age, **159**,
44-45 (1947) Jan. 16.

Procedures for tinning cast iron by
use of the new fused salt baths are de-
scribed. Process is said to result in
better adhesion than the older meth-
ods and to give smoother and more
continuous coatings.—BLR.

**"Ucilon" Organic Coating Pro-
vides High Corrosive Protection.**
Machinery, **53**, 7, 185 (1947) Mar.

New organic coating material for-
mulated to provide extremely high re-
sistance to wide variety of corrosive

conditions has been developed by United Chromium, Inc. This coating, designated "Ucilon," is resistant to acids, alkalies, and salts, and is unaffected by oils, gasoline, and alcohols, including vegetable and fish oils, commercial alcohols, lubricating oils, greases, and other petroleum derivatives. It remains flexible and tough enough to withstand abrasion and moderate flexing over a wide range of temperatures, but is not recommended for service at temperatures above the boiling point of water for extended periods of time. Coatings adhere firmly to properly prepared metal, wood, and concrete surfaced.—INCO.

Maintenance of Oil Field Equipment. D. R. HISKEY, Corrosion **2,** 7 235-47 (1946) Nov.

Some of the new materials developed during the war for the protective coating of oil-field equipment are discussed. Proper preparation of metal surfaces, bonding, and various types of metal primers are also discussed. The necessary requirements of a coating are good bonding with the base metal, imperviousness to water, ease of application, sufficient plasticity to conform to irregularities on the metal surfaces, and incorporation of a chemical rust inhibitor. Each point is discussed in detail.

Marine Corrosion and Fouling. II. H. W. RUDD, Paint Mfr. **16,** 391-7 (1946) Nov.

Various copper compounds used in anti-fouling coating compositions are discussed as well as anti-corrosion coatings in general.

Rust Protection by Galvanizing. Durability of Electrolytically Galvanized Pipes and Armatures in

Cold and Hot Water. H. KRAUSE. Anz. Machinenwesen, **66,** 10, 3-4 (1944) ; Chem. Abs., **40,** 7143 (1946).

The action of zinc as a protection against rust and the use of electrically heated galvanizing baths for pipes are discussed. Galvanic galvanizing possesses essential advantages over hot galvanizing, but only if the coating applied is not too thin.—INCO.

The Influence of Textures and Composition of Surface on the Attachment of Sedentary Marine Organisms. C. M. POMERAT AND C. M. WEISS, Biol. Bull., **91,** 1, 57-65 (1946) Aug.

Submerged samples of plastics, woods, glass, coated woods, steel, paint and plastic-coated steel, galvanized iron, nickel, Monel, lead, zinc and galvanized iron pipe were submerged as substrates for 3 months in Biscayne Bay, Miami, for collection of sedentary populations. Purpose was to study the effect of surface irregularities and subtrate compositions. Results suggest that efficiency of substrate as a fouling collector is in general correlated with porosity of surface or with fibrous nature of surface. Smooth, non-porous, non-fibrous surfaces, especially if also hard, seem to be poor accumulators of sedentary organisms. Many fish eggs were found on Monel. Zinc was actively corroded. Barnacles were easily removed from the galvanized iron. The weight and number of barnacles are given for each composition.—INCO.

Pocket-Type Adhesion Tester for Organic Coatings. R. J. PHAIR. Bell Lab. Rec. **24,** 443-444 (1946) Dec.

Describes instrument which measures adhesion by determining pressure

that has to be applied to a scratching tool in the instrument to make it expose the base material under the finish.—BLR.

A New Chemical Coating to Protect Metals. Chem. Ind., **59,** 1001 (1946) Dec.

Describes development and application of a unique polyvinylbutyral resin-phosphoric acid wash primer for reduction of atmospheric corrosion losses.—BLR.

Rusting and Painting Trouble Corrected. F. A. WESTBROOK, Ind. *Fin.,* **23,** 82 + (1946) Dec.

Concerns problem in connection with the finishing of 8-inch pressed steel shells for commercial product-filters. Trouble arose when the company was relying upon four outside concerns to manufacture steel shells for its filters.—BLR.

FUNDAMENTALS

Some Aspects of the Corrosion of Aluminum. P. F. THOMPSON, J. Council Sci. Ind. Res. **19,** 157-165 (1946); Chem. Abs. **41,** 80 (1947).

The corrosion of aluminum and its relation to film formation are discussed with special reference to corrosion in aircraft engines. Mechanical breakdown and repair of the surface film have been followed electro-chemical measurements. The film is repaired by the products of two types of corrosion, "differential aeration" and "hydrogen evolution." The calculated limit of hydrogen evolution coincided with definite inflections of the potential-temperature curves. Aluminum is also corroded by copper-ion

discharge which initiates continuous hydrogen evolution. Visual observations were made of hydrogen evolution on aluminum and magnesium abraded in neutral liquids. The effects of minute abrading movements in machines and structures in initiating corrosion are discussed.—INCO.

Diagram for the Process of Corrosion. N. D. TOMASCHOV, J. Gen. Chem. Russ., **12,** 585-587 (1942); Brit. Abs., **BI,** 341 (1946) Oct.

Information regarding a corrosion process may be represented diagrammatically by means of a succession of ring sectors of different widths around the circumference of a a circle. Each stage of the process, e.g., ionization of the metal, motion of ions in solution under the action of an electric field, formation and disengagement of hydrogen bubbles at the cathods, etc., is cosidered as having a "resistance" corresponding with the width of the ring sector representing it. Some steps are in parallel. The scheme is compared with a branching electrical circuit. The speed of the corrosion process is determined, basically, by that of the step with the least speed, in series combination, and by that with the greatest (or least resistance), in parallel combination.—INCO.

Effect of Lead in Hot-Dip Galvanizing Baths. W. G. IMHOFF., Iron Age, **159,** 46-49 (1947) Jan. 9.

Use of sufficient lead is said to result in a thin fluid bath and smoother, more lustrous coatings. Cites several instances in which lead additions helped correct galvanizing difficulties. Reviews sources of lead in spelter.
—BLR.

GENERAL CORROSION

The Corrosion of Metals. VI—The Corrosion of Copper and Its Alloys (continued). Sheet Met. Ind., **24,** 145-151 + (1947) Jan.

Deals with all aspects of corrosion of copper-nickel alloys; corrosion of copper alloys by steam and condensate; atmospheric corrosion of copper; copper-beryllium alloys; aluminum bronzes. Consideration of copper alloys in this series began ibid., **23,** 2159-2164 (1946) Nov.—BNF.

Aluminum Alloy 75S. Mach. Design, **19,** 143-145 (1947) Jan.

Gives properties; physical constants; characteristics; applications; fabrication; heat treatments; resistance to corrosion; galvanic corrosion; corrosion-resistant finishes; material designations.—BLR.

Oxidation Resistant Alloys. BENJAMIN LUSTMAN, Steel, **120,** 68-69 + (1947) Jan. 20.

Theory of oxidation of metals and alloys, including rate equations for the different types, is discussed. Also discusses the structure of scales formed on oxidation, and methods for determining oxidation resistance. Relevant facts concering several common types of alloys are discussed.—BLR.

Corrosion of Eliktron AM 503 in Contact with Other Metals. C. J. BUSHROD, Magnesium Rev. and Abs., **6,** 67-75 (1946) July.

Investigation of corrosion of AM-503 (in air or 3% sodium-chloride) when coupled with stainless steel, cadmium-plated steel, Duralumin (bare or anodised); similarly of corrosion of sheet AM503 riveted to Duralumin or MG7 with MG5 rivets; and of corrosion-inhibiting effects of various paints and joining compositions in use with composite AM503/Duralumin specimens.—BNF.

Physico-Chemical Problems of Metallic Surfaces. P. BASTIEN, Mem. Soc. Ing. Civ. France, **98,** 344-356 (1945); Brit. Abs., **BI,** 340 (1946) Oct.

Theoretical and practical aspects of the structure and properties of metal surfaces are reviewed and the techniques of metallographic and electron microscopy, X-ray and electron diffraction, used to examine such surfaces are described. Corrosion, wear, friction and lubrication, reflective power, strength, etc., are correlated with the physico-chemistry of the metal surface, which is regarded as an oriented, multicrystalline aggregate having directional properties and moderately strong ambient field of force. Surface phenomena produced through fusion, plastic deformation, and machining or abrasion of metals are discussed as the mechanics of adsorption.—INCO.

Metals in Modern Society—Fundamental Research on Metals and Alloys a Must. C. S. SMITH, Inst. for Study of Metals, Univ. of Chic. Min. & Metall. **27,** 479, 541-543 (1946) Nov.

Metallurgists' at present are too closely tied to industrial applications and have failed to gain basic understanding of metals and alloys. The newly-founded Inst. for the Study of metals at the University of Chicago will associate with physicists interested in the theory of the solid state, and
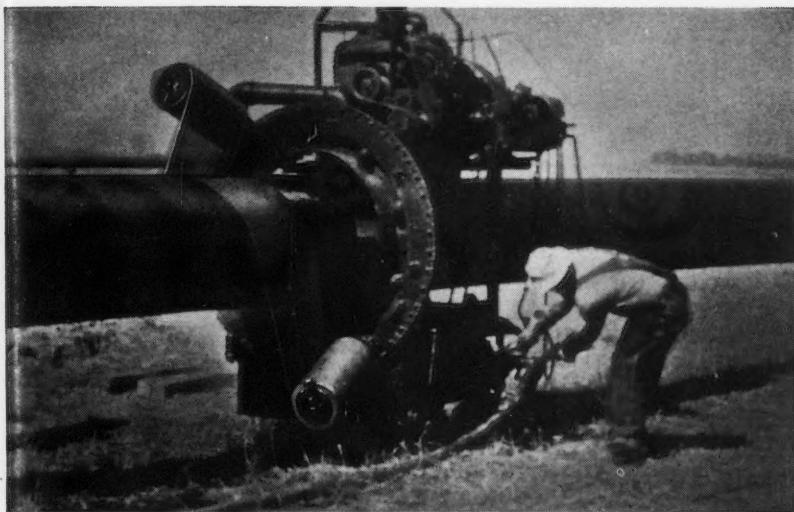
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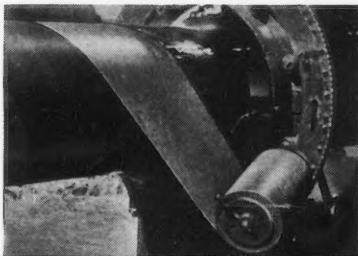
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with chemists concerned with understanding the nature of reactions of metal surfaces with non-metallic media. A particular feature will be the low-temperature laboratory, work being planned on the magnetic, elastic, structural and thermal properties of metals down to temperatures of liquid helium and below, as well as high strength properties.—INCO.

Factors Influencing the Pearlitic Micro-Structure of Annealing Hypoeutectoid Steel. R. A. Grange, ASM Preprint 26, 20 pp. (1946).

Pearlitic microstructure developed by comparable isothermal annealing of each of twelve types of aluminum-killed hypoeutectoid steel was investigated. Results indicate that character of pearlite in an annealed steel is somehow controlled by the interrelated factors: composition, thoroughness of deoxidation, and austenite grain size just prior to transformation. In a number of modern types of steel it appears necessary, if an annealed structure of well-formed pearlite is desired, to raise the austenitizing temperature well above that ordinarily used in present commercial practice, at least unless considerable prior cold working is feasible.—BLR.

Grain Boundary Penetrations by Liquid Metals. II.—Attack of Platinum Alloy Sparking Plugs by Molten Lead. P. J. E. Forsyth and W. R. Smith, Metallurgia, **34**, 245-246 (1946) Sept.

Attack by lead arising from use of leaded fuels. Part I of this series (ibid., 34, 186-188 (1946) Aug., dealt with service failures due to the contact of molten metals with stressed parts.—BNF.

Stress-Corrosion Cracking of Mild Steel. VIII. Discussion of Contributed Criticism. J. T. Waber and H. J. McDonald, Corr. & Mat. Prot. **3**, 8, 13-20 (1946) Oct.-Dec.

Discussions and criticisms by various individuals of the author's theory of stress-corrosion cracking of mild steel are answered.

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